ADA051129

Report No. FAA-AEQ-77-16

HIGH ALTITUDE POLLUTION PROGRAM

A STATUS REPORT PREPARED IN ACCORDANCE WITH PL 95-95

DEPARTMENT OF TRANSPORTATION
UNITED STATES OF AMERICA

D D C
RECEIVED
MAR 10 1978
F
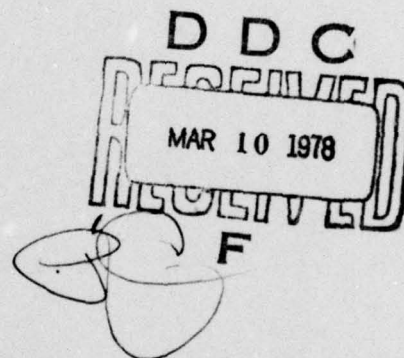
December 1977

U.S. DEPARTMENT OF TRANSPORTATION
Federal Aviation Administration
Office of Environmental Quality
High Altitude Pollution Program
Washington, D.C. 20591

1. Report No. (14) FAA-AEQ-77-16	2. Government Accession No.	3. Recipient's Catalog No. (11)
4. Title and Subtitle (6) High Altitude Pollution Program A Status Report Prepared in Accordance with PL 95-95		5. Report Date December 1977
		6. Performing Organization Code AEQ-10 ?where
7. Author's (10) N. Sundararaman		8. Performing Organization Report No.
9. Performing Organization Name and Address U.S. Department of Transportation Federal Aviation Administration, Office of Environmental Quality, High Altitude Pollution Program Washington, D.C. 20591		10. Work Unit No. (TRAIS)
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address (12) 36p.		13. Type of Report and Period Covered Status Report as of December 1977
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The past and planned activities of the High Altitude Pollution Program (HAPP) are summarized. A preliminary HAPP assessment of the stratospheric effects from aviation indicates that there is no imminent threat of ozone reduction from any type of existing aircraft, though substantial uncertainties still remain to be unravelled.

D D C

MAR 10 1978

F

17. Key Words Stratospheric Pollution, Aircraft Cruise Emissions, Ozone Depletion, Nitrogen Oxides from Aircraft	18. Distribution Statement		
19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price

Form DOT F 1700.7 (8-72)   Reproduction of completed page authorized

i 406 862

TABLE OF CONTENTS

ii

1. INTRODUCTION

The subject of high altitude pollution from aircraft is a complicated
one. Since 1970, when the Department of Transportation requested
Congress to authorize a study of possible climatic effects from
SSTs, the Department has led Federal efforts to understand the
impact of high altitude aircraft operations on stratospheric ozone.
In March of 1971, Congress voted not to continue funding the development
of a civil supersonic transport aircraft, in part because of
questions regarding possible adverse effects of SSTs on climate. A
few months later, Congress authorized the Department to carry out
the Climatic Impact Assessment Program, which came to be called
"CIAP." Part of the funds appropriated for CIAP were used to
support an independent study by the Climatic Impact Committee of
the National Research Council (NRC). The final reports of these
studies (1, 2) were issued in early 1975. It is partly because of
the Department's efforts that the potential impact of effects from
fluorocarbons, fertilizers, nuclear weapons tests and other chemical
pollutants can be understood and appreciated.

The CIAP report concluded that continued, rapid growth of long-
range, high altitude aircraft flights could have potentially serious
environmental effects. It also stressed, however, that the problem
is, fortunately, not yet at the serious stage. If we act promptly --
and we are, giving the matter high priority -- we can avoid environmental
degradation, while at the same time provide the growth in aviation
services demanded by a healthy economy. Though the report of the
NRC Climatic Impact Committee differed somewhat on a few specific
technical details, it essentially confirmed the CIAP conclusions.

With the publication of the CIAP findings in January 1975, came the
announcement by the Federal Aviation Administration (FAA) that a
high altitude pollution study would be developed as a part of the
total environmental program of the agency. Since CIAP was a wide-
ranging multidisciplinary "technology assessment," as directed in
the enabling legislation, it did not provide all the data needed to
judge at what time there might exist a need for regulation of
stratospheric flight. That is what the FAA's High Altitude Pollution
Program (HAPP) is to do. Specifically, its objective is "to quantitatively
determine the requirements for reduced cruise-altitude emission
and, in conjunction with the Environmental Protection Agency and
the International Civil Aviation Organization, to ensure that, if
necessary, appropriate regulatory action is taken to avoid environmental
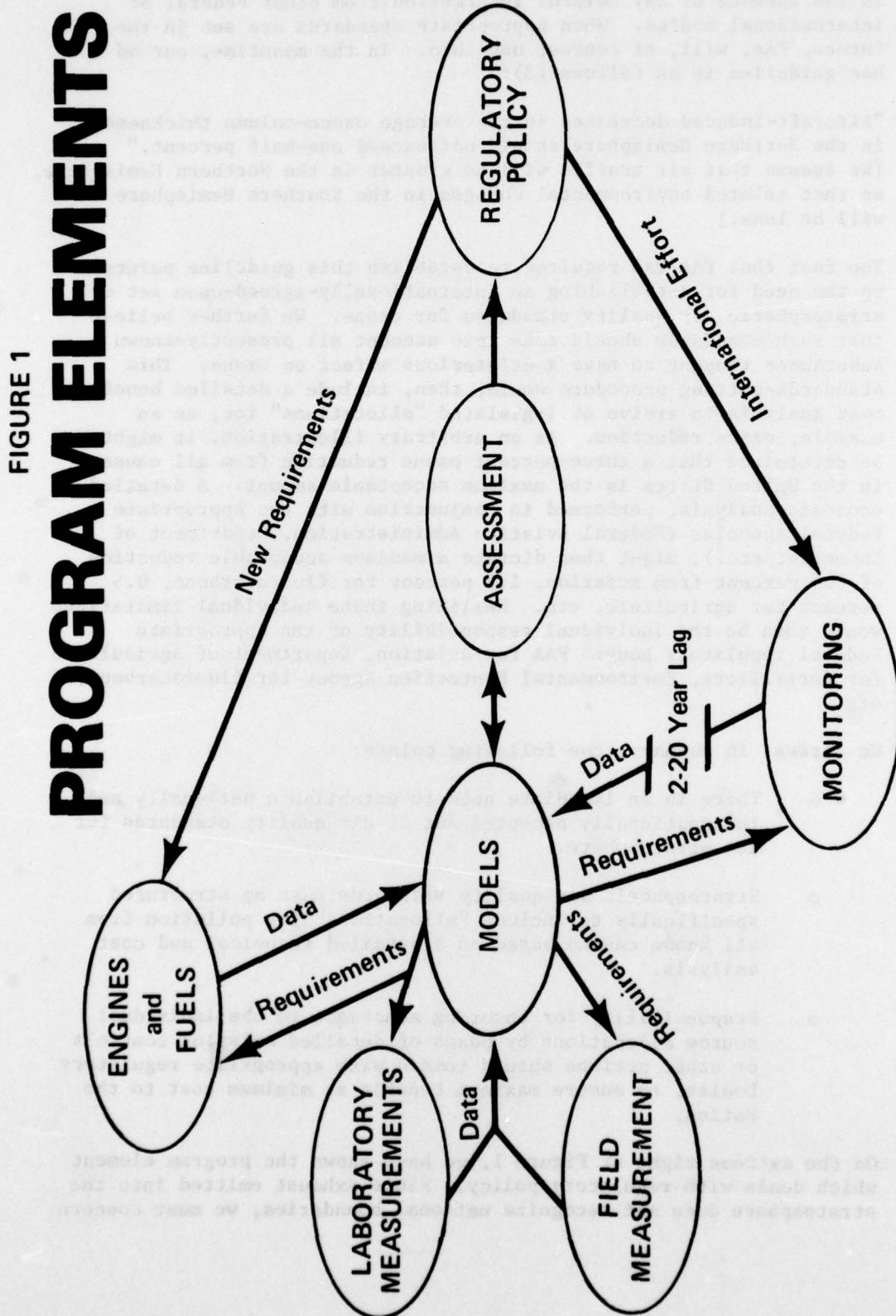degradation" (3).

The concerns regarding stratospheric flight fall into two main
categories: likely changes in stratospheric ozone amounts and
possible climatic effects. The nitrogen oxides (nitric oxide and

1

nitrogen dioxide) in the aircraft exhaust could theoretically
reduce stratospheric ozone through a series of chemical reactions
in which the nitrogen oxides themselves are regenerated until their
eventual removal by chemical and transport processes. Sulfur
dioxide (through forming aerosols), water vapor and the nitrogen
oxides could affect the climate, directly or indirectly, by altering
the radiation transfer processes in the atmosphere. With this
background of concerns, FAA has moved expeditiously to structure a
program to provide the basis for policy decisions in regard to the
need for, timing of, and type of regulations. This is the only
Federal program specifically directed to the concerns of stratospheric
pollution by aircraft (4).

2.   HAPP PROGRAM ELEMENTS

The program is organized under seven major areas of work (see
Figure 1). In order to answer a first priority question: "What is
the immediacy of need for regulation?," we have, in the past 9 to
12 months, expanded upon the data on engine emissions, particularly
with respect to the amount at various flight cruise altitudes, for
the fleet operations we project through 1990. These are inputs to
one-and-two dimensional stratospheric models. The output will
identify the resulting impact on ozone and climate. Associated
with this work is a definition of the uncertainties relating to the
inputs as well as the capabilities of the models. This is why we
see at the center of the program a need to maintain and continually
update our capabilities to use the best models available. These
complex computer-based representations are our best understanding
of the relationship between cause and effect and are our only means
of projecting quantitatively the likely consequences of future
actions. Laboratory work is required to maintain an accurate
technical data base on important chemical reactions. Reliable
field measurements of concentrations of key atmospheric gases are
also needed, both to verify, and to provide input data to, the
mathematical models. There is a "back-and-forth" exchange among
all of these elements. While the primary utility of models is to
diagnose atmospheric behavior and make projections, they are also
used in studies which determine where the greatest uncertainties
lie. This "feedback" process goes on continually, providing guidance
in regard to optimum expenditure of our resources.

The models tell us what the expected physical result of emissions
from a given fleet would be, but assessment of the significance of
that result is another matter. It is clearly not the responsibility
of the FAA to make either implicit or explicit judgments regarding
the "permissibility" of a given amount of environmental pollution.
That responsibility has been delegated to other agencies, or falls
within purview of Congress. Thus, the FAA's assessment of the
"significance" of environmental effects projected by the use of
models must be made with respect to a prescribed air-quality standard
which we do not now have for the stratosphere. Since these environmental
protection efforts must have a framework within which goals are set
and assessments are made on at least a preliminary basis, the FAA
has initiated HAPP using, admittedly arbitrary, guidelines. We

FIGURE 1

PROGRAM ELEMENTS

Figure showing program elements: REGULATORY POLICY, ASSESSMENT, MONITORING, MODELS, ENGINES and FUELS, LABORATORY MEASUREMENTS, FIELD MEASUREMENT, connected by arrows labeled "International Effort", "New Requirements", "Data", "2-20 Year Lag", "Requirements", "Data", "Requirements".

stress that these are meant only for the purposes of this program, in the absence of any helpful information from other Federal or international bodies. When appropriate standards are set in the future, FAA, will, of course, use them. In the meantime, our ad hoc guideline is as follows (3):

"Aircraft-induced decreases in the average ozone-column thickness in the Northern Hemisphere should not exceed one-half percent." (We assume that air traffic will be greater in the Northern Hemisphere, so that related environmental changes in the Southern Hemisphere will be less.)

The fact that FAA was required to establish this guideline points up the need for establishing an internationally-agreed-upon set of stratospheric air quality standards for ozone. We further believe that such standards should take into account all presently-known substances thought to have a deleterious effect on ozone. This standards-setting procedure would, then, include a detailed benefit-cost analysis to arrive at legislated "allocations" for, as an example, ozone reduction. As an arbitrary illustration, it might be determined that a three-percent ozone reduction from all causes in the United States is the maximum acceptable amount. A detailed economic analysis, performed in conjunction with the appropriate Federal agencies (Federal Aviation Administration, Department of Commerce, etc.), might then dictate a maximum acceptable reduction of 0.5 percent from aviation, 1.5 percent for fluorocarbons, 0.5 percent for agriculture, etc. Realizing these individual limitations would then be the individual responsibility of the appropriate Federal regulatory body: FAA for aviation, Department of Agriculture for fertilizers, Environmental Protection Agency for fluorocarbons, etc.

We stress, in summary, the following points:

o   There is an immediate need to establish a nationally and internationally accepted set of air quality standards for the stratosphere.

o   Stratospheric air quality standards must be structured specifically to include "allocations" for pollution from all known causes based on a detailed technical and cost analysis.

o   Responsibility for ensuring adherence to the individual source allocations by means of detailed emission controls or other actions should remain with appropriate regulatory bodies, to ensure maximum benefit at minimum cost to the Nation.

On the extreme right of Figure 1, we have shown the program element which deals with regulatory policy. Since exhaust emitted into the stratosphere does not recognize national boundaries, we must concern

ourselves with both national and international coordination of our actions. We appreciate at the outset the importance of this coordination function.

Finally, a few words about monitoring. Simply stated, we define "monitoring" as a long-term series of measurements of something, for the purpose of detecting trends in its average value. To make a simple analogy, you can <u>measure</u> automobile gas mileage on one tank of gas. But in order to tell whether your engine is properly tuned, you need to <u>monitor</u> your gas mileage by frequent measurements to be able to see when it starts to degenerate. Atmospheric monitoring is a complex, long-term effort. Monitoring of stratospheric effects, if it is to be useful, must also be a well-coordinated, international undertaking. We see our job as one of insuring that aviation-related concerns are adequately addressed in National Aeronautics and Space Administration (NASA), National Oceanic and Atmospheric Administration (NOAA) and other on-going programs.

In Figure 2, we illustrate the administrative organization of our program. We are in the process of formally establishing a technical advisory group. This will be a small group principally made up of leading working scientists and engineers. We will look to the group for guidance in apportioning our research efforts and appraising the significance of our results (4).

3. <u>FY 1976, 1976T AND FY 1977 EFFORTS</u>

Brief summaries of the HAPP efforts in FY 1976, 1976T and FY 1977 are given in Table 1.

4. <u>PROCUREMENT PLAN FOR FY 1978</u>

The HAPP procurement plan for FY 1978 is given in Table 2. Note that many of the studies cited in Section 3 (preceding) have been funded in previous years for work to be performed in FY 1978. Thus, the procurement plan does not represent an all-inclusive list of work to be performed in FY 1978.

5. <u>CURRENT STATUS OF THE ASSESSMENT OF THE STRATOSPHERIC EFFECTS FROM AVIATION</u>

The chemical and physical processes which determine atmospheric ozone concentrations are very complex and involve a number of substances, both natural and anthropogenic.

a. <u>Chemical Processes:</u>

Just the known important reactions alone, relevant to stratospheric ozone chemistry, number well over a hundred, among several dozen different chemical trace species. To the extent presently known, these species can be grouped into four categories: the oxygen-based, water-based, chlorine-based and nitrogen-based (the so-called O_x, HO_x, ClX, and NO_x, respectively) systems. The nitrogen oxides mentioned earlier are part of the NO_x system.

FIGURE 2

ADMINISTRATIVE ORGANIZATION

NATIONAL/INTERNATIONAL COORDINATION

Policy Development and Review

Environmental Quality

High Altitude Pollution Program

- ◆ Assessment
- ◆ Regulatory Policy

Advisory Board

Contractors

- ◆ Atmospheric Models
- ◆ Engine Emissions & Fuels
- ◆ Laboratory Chemistry
- ◆ Field Measurements
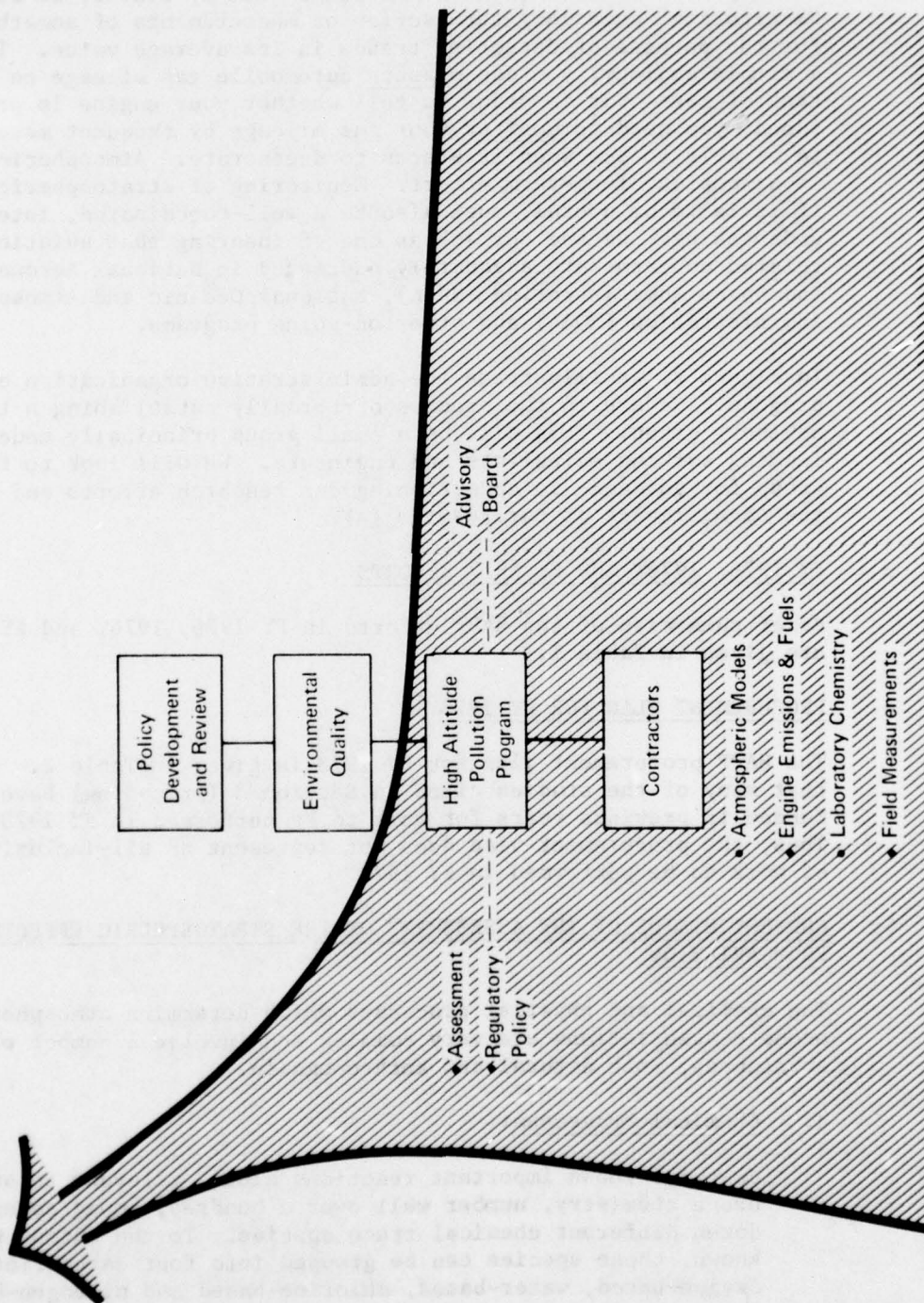
TABLE 1

HAPP Studies Through FY 1977

Procurement Title	Principal Investigator(s)	Performing Organization
Numerical Simulation of Atmospheric Response	F. Luther	Department of Energy/Lawrence Livermore Laboratory
Two-Dimensional Model Studies	G. Widhopf	U.S. Air Force/Space and Missile Systems Organization: Aerospace Corporation
Numerical Simulation of Atmospheric Response and Ozone Data Analysis	F. Luther J. Lovill	Department of Energy/Lawrence Livermore Laboratory
Two-Dimensional Model Studies, Amendment	G. Widhopf	U.S. Air Force/Space and Missile Systems Organization: Aerospace Corporation
Two-Dimensional Model Studies, Modification	G. Widhopf	U.S. Air Force/Space and Missile Systems Organization: Aerospace Corporation
Numerical Simulation & Ozone Data Analysis: Amendment 1	F. Luther J. Lovill	Department of Energy/Lawrence Livermore Laboratory
Development of an Objective Methodology for Determining Stratospheric-Tropospheric Mass Exchange	E. Danielsen	Oregon State University
Refinement & Modification of the Crutzen 2-D Model of the Stratospheric Ozone Balance	P. Crutzen	Colorado State University
Study of Atmospheric Mechanisms	G. D. Robinson	Center for Environment & Man
Numerical Simulation & Ozone Data Analysis: Modification	F. Luther J. Lovill	Department of Energy/Lawrence Livermore Laboratory
Stratospheric Emissions from Aircraft Operations	P. Athens	Environmental Protection Agency/ A. D. Little Co.

7

TABLE 1 (continued)

Procurement Title	Principal Investigator(s)	Performing Organization
Analysis of Fuel Usage	P. J. Zegan	Eastern Air Lines, Inc.
International Air Traffic Forecast	R. J. Pozdena	Stanford Research Institute
Reaction Rate Data, Tabular Input*	D. Garvin	National Bureau of Standards
Measurement of $O(^1D)/N_2O$ & HNO_2/O_3 Kinetics	A. Fontijn	Aerochem Research Laboratories
Laboratory Study of Chemical Reactions	E. W. Kaiser	Ford Motor Company
Heterogeneous Decomposition of Ozone on Sulfuric Acid at Stratospheric Temperatures	A. Harker	Rockwell International
Laboratory Study of Chemical Reactions	H. Schiff	York University
NO_2 Photolysis	J. Davenport	Stanford Research Institute
Laboratory Chemistry Studies	D. Kley	National Oceanic and Atmospheric Administration: Aeronomy Laboratory
Laboratory Study of HO_2 Kinetics	B. Thrush	University of Cambridge
Analysis of Measurement Requirements	R. Penndorf	Dr. R. Penndorf, Consultant
Critical Analysis of Field Measurement Data	R. Penndorf	Dr. R. Penndorf, Consultant
Cooperative Stratospheric Aerosol Research Program	D. J. Hofmann	University of Wyoming
Processing, Reduction, and Data Analysis of April & May 1975 CIAP/Airstream Data	P. R. Guthals	Department of Energy/Los Alamos Scientific Laboratory
Balloon Launch, Tracking, & Recovery Costs for NO Detector Flight to 45 km	Comm. W. Smith	Office of Naval Research

8

TABLE 1 (continued)

Procurement Title	Principal Investigator(s)	Performing Organization
Measurement to 45 Kilometers Using Cryogenic Sampling & Other Techniques	L. Heidt P. Wilkness	National Center for Atmospheric Research/National Science Foundation
Development of Advance Instrumentation (tunable double heterostructure laser diodes)*	F. Allario	National Aeronautics and Space Administration/ Langley Research Center
Data Interpretation on Measurements of Trace Gases	D. G. Murcray	University of Denver
Measurement of Stratospheric Water Vapor*	J. Mastenbrook	Naval Research Laboratory
Development of Stratospheric Measurement System	N. Macoy/S. Poultney	Perkin-Elmer Corporation/ Electro-Optical Division

* Funded jointly with the Office of Upper Atmospheric Research, Office of Space Sciences, National Aeronautics and Space Administration.

9

TABLE 2

HAPP PROCUREMENT PLAN (FY 1978)

Program Element	Estimated Cost ($1,000)
1. Modeling	
a. 2-D Model Studies	100
b. Consistent Set of Input Data	95
2. Engines and Fuels	
a. Engine Projections	150
3. Laboratory Measurements	
a. Chemistry and Photochemistry of Pernitric Acid	100
b. Photochemical Studies of O_3 and H_2CO	100
c. Chemical Kinetics of $CH_3 + O_2$, $CH_3 + O_3$, and $OH + ClO$	100
d. Heterogeneous Removal Processes	90
4. Field Measurements and Monitoring	
a. Analysis of Block 5D Ozone Data	125
b. Intercomparison of Ozone Measurement from Dobson Instruments	60
c. Development of Advance Laser Diode Instrumentation	50
d. Direct Measurement of Nitric Oxide in the Upper Atmosphere	50
e. Aircraft Measurements of Soluble Gases	200
f. Development of Balloon-Borne Measurement of H_2O_2	95
g. Comprehensive Analysis of Experimental Data as Related to the Requirements of HAPP	90
h. Coordinated Measurements of Trace Gases in the Stratosphere	145
i. Test Flight for HAPP Stratospheric Measurement System	300
j. Measurement of Stratospheric H_2O	180
k. Intercomparison of Rocketsonde Ozone Measurement	50
l. Analysis of Trace Gases in Cryogenic Air Samples	90
m. Stratospheric Measurement of HO_2	150

TABLE 2 (continued)

Program Element	Estimated Cost ($1,000)
5. Assessment, Regulation and Coordination	
a. Technical Analysis of Model Results	300
b. Documentation	50
c. High Altitude Pollution Program Studies	120
d. HAPP Document Catalog	9

11

There are complex competing relationships among the various ozone production and destruction reactions, some of the species (e.g. NO_x) leading to formation of ozone through the well-known "smog" reactions at low altitudes (up to about 25 km or so) or to ozone destruction through catalytic chain reactions at higher altitudes (mainly in the middle stratosphere and above). Furthermore, the species of one system may react with those of another, leading to "feedback" loops in the chemistry and thus either to reducing or enhancing the impact of a given trace species.

Given a number of reactant molecules, the effectiveness of a chemical reaction between them can be expressed through a quantity known as the chemical reaction "rate constant." The rate constants are important input data for the atmospheric models, and information regarding a crucial rate constant has become available only recently: through the efforts of the National Oceanic and Atmospheric Administration, the rate constant for the important reaction of the perhydroxyl radical (a member of the HO_x family) with nitric oxide (a member of the NO_x family) has been measured to be about <u>forty times faster</u> than was assumed during the CIAP studies. This measurement (5) has also been confirmed by several independent studies. Using the new value for this rate constant, the calculated effects of aircraft are substantially reduced from those expected at the end of the CIAP and National Research Council efforts. A detailed discussion of this finding is to be found in the Appendix to this report. However, we have to await the results of the on-going laboratory determinations of a relatively small number of rate constants before we can fully accept the implications of this finding.

b. Physical Processes:

So far we have considered only the results of improved--and improving--chemistry in the models. The study of aircraft effects on ozone is considerably different from that of, for example, fluorocarbons in regard to the importance of assumptions made about atmospheric transport. Much of the important NO_x injection from aircraft takes place between about 10 and 18 km. This is the region of the atmosphere where ozone concentrations are almost entirely controlled by transport (as opposed to chemistry) and also where transport uncertainties are greatest.

Any model which seeks to assess the amount of ozone destruction associated with aircraft-NO_x injections must account for the rate at which the NO_x is removed (upward or downward) from the region of injection. Simplistically, on a global-average scale, upward transport from aircraft flight altitudes toward

the region of high ozone concentration will result in ozone destruction, while downward or quasi-horizontal transport has the opposite effect. Thus, transport uncertainties can place a fundamental limit on our quantitative understanding of aircraft effects.

An effort has been initiated under the sponsorship of the High Altitude Pollution Program to develop an objective methodology for the calculation of actual stratospheric-tropospheric mass exchange by exploitation of the "tracer" characteristics of a purely meteorological quantity called "potential vorticity." It is expected that development of this data set, using worldwide 12-hourly radiosonde data, will provide a truly meaningful data base for use in the development and test of models which more realistically represent transport in the region of the tropopause. The task is a difficult and challenging one, which will take several years.

c. Present Understanding of Aircraft Effects

So far this discussion has focused on NO_x effects on ozone. What about those of water which can lead to formation of the members of the HO_x system? The fact that ozone is less sensitive to NO_x increases than previously believed means it must be more sensitive to other perturbations. The ClX species have taken up some of the "slack," and HO_x has absorbed the rest. Thus, detailed evaluation of perturbations to ozone from water in aircraft exhaust needs to be considered once again.

With the limitations we have described here in mind, we note the conclusions we believe may be drawn (6):

1. Realistic projections to 1990 of air traffic growth for the world subsonic fleet of aircraft indicate that ozone is not likely to be significantly affected by those aircraft, with a marginal increase in ozone now being actually predicted.

2. Furthermore, analysis of the effects of subsonic aircraft emissions (i.e. those below a nominal 15-km altitude) indicates, contrary to previous studies, that given our present understanding subsonic aircraft-NO_x emissions cannot forseeably result in ozone reduction irrespective of fleet size (within reasonable bounds).

3. Earlier estimates of ozone reduction from supersonic transport emissions of NO_x at 17 to 20 km appear to

13

have been substantially in error. Based on one-dimensional models, which include relatively complete chemistry but treat transport in a highly parameterized fashion, our present understanding leads to predicted ozone perturbations of an absolute magnitude markedly smaller than given in previous studies (1, 2) and outside their ranges of estimated uncertainty (factors of ±2 to ±10 depending upon the altitude of emission).

4. It is questionalbe whether NO_x emissions from "Concorde-like" supersonic transports (SSTs) (flying at about 17 km) reduce ozone at all. Present results, from models which consider both tropospheric and stratospheric chemistry, indicate that they do not.

5. The effect of NO_x emissions from aircraft cruising at 20 km is in doubt, though small ozone reductions for very large fleets of such aircraft are still predicted by some models.

6. There is a crucial need for more data on trace constituents in the atmosphere (especially simultaneous measurements of NO_x species, and measurements of HO_x species), for laboratory measurements of critical chemical reaction rates, for development and use of uncertainty analysis tools, and for a better understanding of transport in the 10- to 20-km altitude region.

In summary, present understanding indicates that there is no imminent threat of ozone reduction from any type of existing aircraft, though substantial uncertainties remain. Thus there appears to be no immediate requirement to develop regulations which would mandate a reduction in cruise-altitude emissions of subsonic or supersonic aircraft. There is a clear necessity for continued study to reduce remaining uncertainties, and to establish a uniform and internationally agreed accurate NO_x emission measurement scheme. Building a framework for regulation (if necessary) of future types of high-altitude aircraft, such as those frequently referred to as a "second-generation SST," or the even higher flying hypersonic transport (HST), is also necessary. Activities of the new International Civil Aviation Organization (ICAO) Committee on Aircraft Emissions should be encouraged to proceed in an orderly fashion along these lines.

d. Aircraft Effluents Relative to Other Threats

Aircraft effluents represent one among a variety of man's potential threats to the ozone shield or to the climate. These various threats, and their unique and common aspects, are summarized in Table 3, from which several points should be noted (7):

14

TABLE 3

A Comparison of Anthropogenic Threats to Ozone and Climate

Source :	Aircraft[1] (cruise)	Aerosol Propellants, Refrigerants, etc.; Space Shuttle[2]	Power Plants[1] (fossil fuels)	Fertilizers[1] (nitrogenous)	Power Plants[1] (nuclear)
Pollutants :	NO_x, H_2O*, SO_x, soot, particulates, CO_2	Fluorocarbons compounds	CO_2, aerosols, N_2O, NO_x, SO_2, H_2O, waste heat	N_2O, NH_3(?)	Radionuclides[5] (Kr^{85}, H^3, C^{14}; waste heat
Ozone column effects:	Increase or decrease	Decrease (potentially large)	Increase slightly, unless N_2O	Decrease(?)	Decrease(?) (NO production)
Climatic effects:	Warming(?)[3]	Warming[4]	Warming (potentially large)	Cooling(?)	?
Pollutant sink altitude:	6-20 km	Surface	Surface	Surface	Surface
Pollutant sink altitude:	~3 km[6]	30-40 km (initial) ~3 km (final)[6]	Surface (oceans, plants)	Stratosphere (initial) ~3 km (final)[6]	Distributed decay
Atmospheric response/ recovery time:	1-5 yr	50-100 yr	100+ (?) yr	10-100 (+) yr	Decades
Special aspects and uncertainties:	Tropopause height, transport, upper troposphere chemistry, sources concentrated by latitude, 2-D, 3-D effects, emission forecasts and measurements	Tropospheric sinks (if any)	CO_2 material balance, equilibrium with oceans, geophysical effects	Unknown sinks for N_2O, equilibration time with N reservoirs	Atmospheric electricity, ions affecting clouds, contrails, transport(?)
Common aspects :	Atmospheric chemistry, transport, climatic phenomena, biospheric impact (if O_3 decreasing)	Atmospheric chemistry, transport, climatic, biospheric impact	Climatic phenomena	Chemistry, transport, biospheric impact	?

1 Principal threat materials (in this context) underlined.

2 The Space Shuttle will introduce chlorine compounds (plus water and NO_x) into the upper atmosphere. Effects relative to halocarbons are thought to be small.

3 Multiple effects: (cooling due to ozone depletion and stratospheric aerosols; warming due to H_2O, contrails, NO_2).

4 Cooling due to stratospheric ozone reduction; warming by tropospheric greenhouse effect.

5 Release depends on reprocessing procedures. See W. L. Boeck, Science, 193, pp 195-198, July 16, 1976.

6 Assumed rainout altitude

* H_2O → Water Vapor; SO_2 → Sulfur dioxide; CO_2 → Carbon dioxide; N_2O → Nitrous oxide; O_3 → Ozone; NO → Nitric oxide; NO_2 → Nitrogen dioxide;

Kr^{85} → Krypton; H^3 → Tritium; C^{14} → Carbon

Source: Oliver, R. C., et al., Private Communication 1977.

1. Aircraft effects, at least for currently projected fleets, have dominant effects in the upper troposphere. An increase in the total ozone column may result from aircraft operations leading to unique and not necessarily desirable effects. The upper troposphere is a region of the atmosphere which is not included in PL 95-95, which is concerned only with the atmosphere above the tropopause; effects in this region are, however, obviously important in any evaluation of world-wide aircraft effects.

2. As indicated earlier, effects of aircraft effluents are particularly dependent on the dynamics and chemistry of the atmosphere near the tropopause. As tropopause height is strongly variable with latitude and season, and aircraft traffic is concentrated in midlatitudes, aircraft effects computations are best handled by models which include both latitudinal and longitudinal dimensions. This is not presently the case, though FAA has initiated efforts in this direction.

3. The recovery time from aircraft effects, should pollutant reduction be found to be necessary, is much shorter (1-5 yr) than is the recovery time for those materials (fluorocarbons) having long lifetimes (50-100 yr) in the troposphere. Any adverse ecological consequence of erroneous decisions would thus be far less long-lasting. Aircraft, of course, have long lifetimes (20 yr) so that any sudden imposition of control measures would have severe economic impacts. Nevertheless, recovery time is an important aspect of any decision-making process.

   While Table 3 does not provide details, it should be noted that the currently projected largest threat to ozone comes from the fluorocarbons. The revisions in chemistry, mentioned earlier, coupled with the addition of previously excluded chemistry have reduced the apparent threat to the ozone column from aircraft NO_x emissions. (These same revisions, however, have led to some increased concern with the effects of aircraft water vapor (H_2O) emissions.) The stratospheric research community has come to recognize the importance of simultaneous and coordinated measurements of chemically-interactive trace species for the verification of the chemical part of stratospheric models. To this end the FAA has initiated efforts aimed at measuring the components of the NO_x system within the same air sample.

   The effects of water vapor emissions depend upon various feedback mechanisms, among which are possible induced alterations of stratospheric H_2O content due to changes in tropopause temperatures. Evaluation of ozone changes and climate changes due to H_2O emissions involves new modeling and data requirements in that sources, transports, sinks, and feedback effects of water vapor are not well

16

understood; the feedback effects involve difficult multidimensional aspects normally associated with climate modeling. In an effort to address the uncertainties existing in modeling atmospheric transport, the FAA is undertaking a feasibility study of a global experiment in which an inert tracer will be injected into the atmosphere near the tropopause and its distribution observed over a sufficiently long interval.

The aircraft question remains, with many uncertainties still evident; these uncertainties are in fact now recognized to be larger, in the strictest technical sense, than they were in December 1974 at the end of the CIAP efforts (since there is now not only a question of how much, but even whether there is an ozone column reduction which may be attributed to aircraft). Reduction in these uncertainties is essential if undesirable ecological consequences on the one hand, or unnecessary economic penalties on the other, are to be avoided. Continued and coordinated effort for their reduction is required.

REFERENCES

1. CIAP, Report of Findings: The Effects of Stratospheric Pollution by Aircraft, DOT-TSC-75-50, Climatic Impact Assessment Program, U.S. Department of Transportation, Washington, D.C., 20590, December 1974.

2. NRC, Environmental Impact of Stratospheric Flight, Climatic Impact Committee, National Research Council of the National Academy of Sciences/National Academy of Engineering, Washington, D.C., 1975.

3. HAPP, Initial Planning Documentation, High Altitude Pollution Program (HAPP), Office of Environmental Quality, Federal Aviation Administration/Department of Transportation, Washington, D.C., 20591, June 16, 1975.

4. Meister, F. A., Associate Administrator for Policy Development and Review (Acting), Federal Aviation Administration, U.S. Department of Transportation, Statement before the Subcommittee on the Upper Atmosphere of the Senate Committee on Aeronautical and Space Sciences, September 8, 1975.

5. Howard, C. J., and K. M. Evenson, Kinetics of HO_2 with NO, Geophysical Research Letters, 4, 10, 437-440, October 1977.

6. Broderick, A., Stratospheric Effects from Aviation, Paper No. 77-799 presented at the American Institute of Aeronautics and Astronautics/ Society of Automotive Engineers 13th Propulsion Conference, Orlando, Florida, July 11-13, 1977. See Appendix for copy of paper.

7. Oliver, R. C., et al., Private Communication, 1977.

APPENDIX
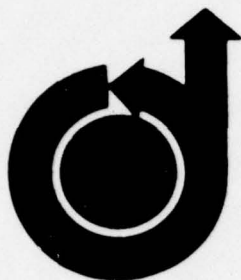
77-799

Stratospheric Effects from Aviation

A. Broderick

U.S. DEPARTMENT OF TRANSPORTATION
Federal Aviation Administration

AIAA/SAE 13th PROPULSION CONFERENCE

Orlando, Florida/July 11-13, 1977

STRATOSPHERIC EFFECTS FROM AVIATION

Anthony J. Broderick
Federal Aviation Administration
Washington, D.C. 20591

Abstract

The findings of four earlier studies (completed around 1975) with regard to effects of high-altitude aircraft are summarized. Highlights of new laboratory measurements are discussed, since several of these new measurements have a major effect on predictions of aircraft effects. The effect of transport in the upper troposphere-lower stratosphere on ozone reduction predictions is reviewed and the difference between fluorocarbon and high-altitude aircraft perturbations in this regard is discussed. The need for, and a new approach to, determining stratospheric-tropospheric mass exchange are presented. A qualitative summary of our best present understanding of aircraft effects on ozone is provided. This shows that, at present, it is not possible to affirm the results of earlier studies in regard to subsonic flight, as it appears that flight at these altitudes will not result in ozone reduction. The case is less definite for SST operations; present results using 1-D models indicate, however, that 17-km flight does not result in ozone reduction, though some models show small ozone reductions from 20-km flight. We hasten to point out, however, that the new data which lead to this conclusion need verification before we can fully accept this important finding. The need for additional work is stressed, especially in regard to development and use of better methods to analyze uncertainty in these complex analyses.

Introduction

Until quite recently, interest in atmospheric ozone was largely academic. More or less regular measurements of this minor constituent of the air, about 90% of which exists in the stratosphere, have been made since the mid-1920s. But during the widely publicized public debate which culminated in the withdrawal of Federal financial support for the development of a commercial supersonic transport (SST), McDonald pointed out that a small reduction in average atmospheric ozone concentration would be expected to lead to an increase in the incidence of skin cancer[1]. At that time, it had already been claimed[2] that the canonical fleet of 500 U.S. SSTs would likely reduce the average ozone amount by a few percent. Fears were also expressed[3] about that time that persistent stratospheric contrails would result from SST operations, effecting a potentially significant cooling of the Earth's surface.

In 1971 the U.S. Congress decided to terminate commercial SST development funding. But the continuing Anglo-French Concorde and Soviet TU-144 development programs, coupled with the general environmental concerns of the period, gave impetus to a cooperative international scientific investigation of the potential seriousness of the environmental problems which had become associated with supersonic flight. Quite early in the formative stages of this effort, it was acknowledged by most scientists that SSTs would only rarely form contrails in the stratosphere, owing to that region's extremely low (typically only a few percent) relative humidity. It was also

pointed out that the earlier calculations concerning ozone reduction by water vapor had been based on unverified assumptions about chemical reaction rates. But the "SST-ozone" problem had not been discounted, since independent work of Crutzen[4,5] and Johnston[6] had laid the foundation for a new source of environmental concern: it was theorized that oxides of nitrogen, present in small amounts in all aircraft exhaust, could reduce ozone. Since material injected directly into the stratosphere resides there for months to years (this "residence time" increasing with height), it was argued that the stratospheric buildup of oxides of nitrogen (NO_x) from SSTs would result in a considerably greater ozone reduction than had earlier[2] been attributed to water vapor emissions. It was on investigation of this phenomenon that the subsequent international efforts were centered.

In the United States, the Department of Transportation Climatic Impact Assessment Program (CIAP) was initiated in August 1971, and a parallel independent effort by the National Academy of Sciences (NAS) was organized shortly thereafter. Technical work on these comprehensive programs was completed by late 1974, and the final reports of the CIAP[6] and NAS[7] studies were released in early 1975. In the United Kingdom, the Committee on Meteorological Effects of Stratospheric Aircraft (COMESA) was formed and conducted a similar study from 1972 to 1975, its report[8] being released some months after the U.S. reports. During this time, the Comite sur les Consequences des Vols Stratospheriques (COVOS) in France also conducted a major study, its final report[9] having recently been made available. In general, the results of these studies were in good agreement. Table 1 shows a summary of their results concerning ozone reduction from SST operations. Note that, to facilitate comparison, we have normalized all input parameters concerning aircraft emission factors (18 g of NO_x per kg of fuel burned), cruise fuel consumption (19,100 kg per hour), flight altitude (16.5 km) and annual cruise time (4.4 hours per day in the stratosphere, 365 days per year--an implicit fleet average aircraft utilization on the order of 8 to 9 hours per day). These values were those concluded by the CIAP study to be realistic, and we characterize the aircraft in this discussion as "Concorde-like" to distinguish it from radically different designs (like that of the 1971 Boeing 2707). We also intend this "normalized" aircraft to broadly represent the TU-144, insofar as its reported characteristics[10] are quite similar.

Table 1: Size of "Concorde-like" SST Fleet (see text) Required to Reduce Average Northern Hemispheric Ozone Concentrations by 0.5% After Several Years of Continous Operation.

Name of Study (Ref)	Number of Aircraft
CIAP (7)	120
NAS (8)	80
COMESA (9)	440
COVOS (10)	330

These studies concerning "SST-ozone" effects carried major implications for subsonic aircraft operations in their final reports. This was particularly true for the CIAP and NAS studies; the COMESA report was not as comprehensive in this regard and the COVOS report presented no quantitative estimates of the subsonic aircraft effect on ozone. Note that the delineation between subsonic and supersonic flight is actually artificial--it is flight altitude which is of concern. Much long-range subsonic flight occurs in the lower stratosphere. Extrapolations of high-altitude (20 km) SST effects to as low as 9 km indicated that subsonic aircraft would also (and presently do) reduce ozone levels. The unit reduction of ozone on a "per-aircraft" basis was calculated to be considerably smaller than that for SSTs, however, primarily because the "residence time" of pollutants injected at such low altitudes was relatively short and high-altitude stratospheric NO_x concentrations would not be so severely perturbed as in the case of SST flight.

The subsonic aircraft results are shown in Table 2 (normalized by us for clarity, as with Table 1). The characteristics assumed for the "1974" subsonic fleet (called the "present" subsonic fleet by CIAP) were as follows[6]: 1,217 "B-707-like" aircraft, with cruise-NO_x emissions of 6 g/kg of fuel burned, average of 5,245 kg/hr cruise fuel consumption; 232 "DC-10/ L-1011-type" aircraft with cruise-NO_x emissions of 15 g/kg of fuel burned, average of 7,482 kg/hr cruise fuel consumption; 232 "B-747-type" aircraft with cruise-NO_x emissions of 15 g/kg of fuel burned, average of 10,219 kg/hr of cruise fuel consumption; all cruising at 11 km for 5.4 hours per day, 365 days per year. For the "747-SP-type" aircraft, "B-747-type" characteristics were assumed, but the cruise altitude assumed was 13.5 km. This produced a major difference in estimated ozone reduction, as shown in Table 2.

Table 2: Estimated Northern Hemisphere Ozone Reductions From Various Postulated Subsonic Aircraft Fleets for Different Studies

Study (Ref)	Percent N. Hemisphere Ozone Reduction
"1974 CIAP Fleet"	
CIAP (6)	0.09
NAS (7)	0.10
COMESA (8)	0.024
COVOS (9)	Not available
100 "747-SP-type" aircraft	
CIAP (6)	0.08
NAS (7)	0.16
COMESA (8)	Not available
COVOS (9)	Not available

Practically speaking, the implications of the findings summarized above were actually far more serious in the near term for the subsonic aircraft fleet than for supersonic aircraft, since the possibility was thus raised that major combustion system redesigns would soon need to be accomplished for a large number of aircraft. At a CIAP-estimated cost of $50 million for research, development and certification of such a system, plus added hardware and maintenance costs, the upper-bound estimate of the total investment

required to keep stratospheric ozone reduction for the CIAP-estimated fleet below 0.5% by about 1990 was placed at about $7 billion (1976 dollars) by one respected airline executive[11]. This was nearly an order of magnitude more than the investment similarly calculated to be required to ensure the same level of environmental protection from the CIAP-estimated "upper bound" SST fleet of that time. Clearly, these matters deserved further study. The "upper-bound" fleet growth projection of CIAP for SSTs was widely discounted as unrealistic, but the same was not so for the CIAP subsonic fleet projection (though it, too, is believed to be overly optimistic).

Further U.S. studies were initiated in 1975[12] by the Federal Aviation Administration (FAA), under its High Altitude Pollution Program (HAPP). The HAPP objective is to reduce the scientific uncertainties in the above described predictions of aircraft effects, in order to develop a solid technical understanding of these factors as a basis for Federal aviation policy development. Similar studies have also been continued in the United Kingdom and France, having been spurred by the February 4, 1976, decision on Concorde[13] and the resulting Tripartite Agreement on Stratospheric Monitoring[14]. As a reference point, Figure 1 summarizes graphically the results of the four "SST studies" briefly described above[15].
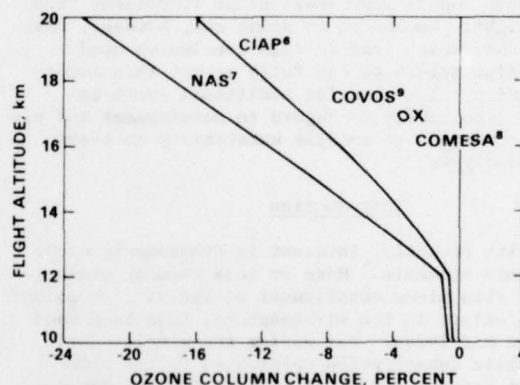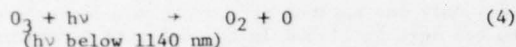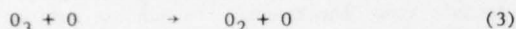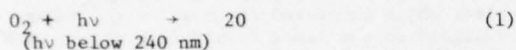
Figure 1: Ozone column change results by various models. The injection rate assumed at each altitude is 1.23×10^9 kg NO_x (as NO_2) per year into a hemisphere. The NAS and CIAP curves are based on 1-D model results, adjusted to correspond to changes to be expected in the "hemisphere" (NAS) or "corridor" (CIAP). Points for COMESA (X) and COVOS (0) are calculated as explained in text (after Oliver et al[15]).

In this paper, we summarize the highlights of the current status of our understanding of the effects of high-altitude flight on ozone. Major factors in our perceptions of important atmospheric chemical reactions are reviewed, as are the relationships between aircraft and fluorocarbon-related stratospheric pollution. Gaps in our knowledge and some of the remaining scientific uncertainties are outlined, and requirements for near-term research presented along with some conclusions.
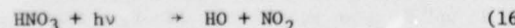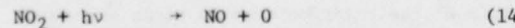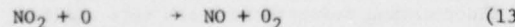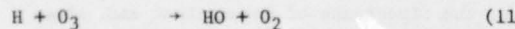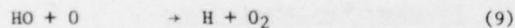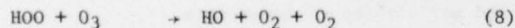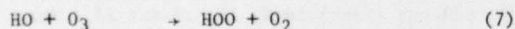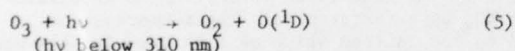
Considerations of Chemistry

In his classic work, Chapman[16] presented a theory explaining the presence of stratospheric ozone (O_3) which relied only on chemical reactions among O_3, oxygen atoms (O) and oxygen molecules (O_2) in the presence of a neutral third body--"M"--fueled by solar ultraviolet energy. This "pure oxygen" chemistry explained how ozone absorbed solar ultraviolet energy ($h\nu$)--thereby shielding the earth from most of this radiation.

$$O_2 + h\nu \rightarrow 2O \qquad (1)$$
($h\nu$ below 240 nm)

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

$$O_3 + O \rightarrow O_2 + O \qquad (3)$$

$$O_3 + h\nu \rightarrow O_2 + O \qquad (4)$$
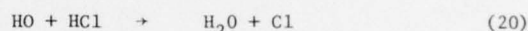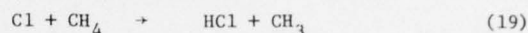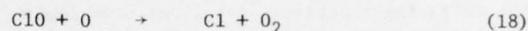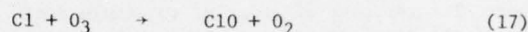($h\nu$ below 1140 nm)

Ozone is destroyed by reaction 3 and reformed by reactions 1 and 2. Reaction 4 usually results in rapid reformation of ozone via reaction 2.

As measurements of ozone improved, it became clear that there was less ozone in the stratosphere than Chapman chemistry alone had explained, and "something else" must account for additional ozone destruction, as clearly shown by Johnston[17]. More than 20 years ago, Hampson, among others, proposed[18] that loss of ozone by reaction with active hydrogen ("water-based" or HO_x) species might be important in this regard, a theory later explored further by Hunt[19]. Logical extensions of this theory--flawed by erroneous assumptions, as mentioned earlier--led to the belief that stratospheric water from SSTs would increase the natural HO_x fraction of ozone destruction, resulting in anthropogenic ozone decreases[2]. At about the same time that the early assumptions in water-based chemistry were re-examined Crutzen[4] and Johnston[5] called attention to the NO_x problem, as summarized earlier. Crudely, the NO_x and HO_x destruction of ozone may be summarized in simplified fashion as follows[7]:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad (5)$$
($h\nu$ below 310 nm)

$$O(^1D) + H_2O \rightarrow 2HO \qquad (6)$$

$$HO + O_3 \rightarrow HOO + O_2 \qquad (7)$$

$$HOO + O_3 \rightarrow HO + O_2 + O_2 \qquad (8)$$

$$HO + O \rightarrow H + O_2 \qquad (9)$$

$$HOO + O \rightarrow HO + O_2 \qquad (10)$$

$$H + O_3 \rightarrow HO + O_2 \qquad (11)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (12)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (13)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (14)$$

$$HO + NO_2 + M \rightarrow HNO_3 \qquad (15)$$

$$HNO_3 + h\nu \rightarrow HO + NO_2 \qquad (16)$$
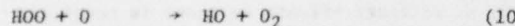
Reactions 6 and 11 are the major sources of hydroxyl radicals (HO), which can also be formed by reaction of excited oxygen atoms $O(^1D)$ with methane (CH_4) and hydrogen molecules (H_2). In turn, the HO reacts with ozone (via reaction 7) to produce perhydroxyl radicals (HOO). Both HOO and HO destroy ozone directly (e.g. reactions 7 and 8) and indirectly by interference with reaction 2 (reactions 9 and 10). In the NO_x cycle, ozone destruction (i.e., in effect, reaction 3) is catalyzed by reactions 12 and 13, with reaction 14 actually leading to small ozone production (via reaction 2) in the upper troposphere and lower stratosphere. Reaction 15 breaks the chain of catalytic ozone destruction formed by reactions 12 and 13 and, since HNO_3 is quite water soluble, is the major "sink" mechanism for stratospheric oxides of nitrogen. (HNO_3 diffuses to the troposphere where it can be removed by rain, usually after thousands of ozone molecules have been destroyed by the original NO_2 molecule.) Note that while HNO_3 is in the stratosphere, reaction 16 serves to demonstrate that HNO_3 only "buffers" the NO_x destruction of ozone, since it may be photolyzed to yield NO_2 and HO.

In the course of these studies it was recognized by Stolarski and Cicerone[20], among others, that chlorine atoms could also "catalyze" ozone destruction by a mechanism parallel to the NO_x cycle:
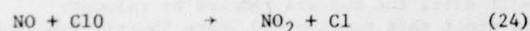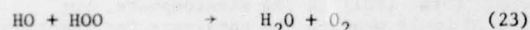
$$Cl + O_3 \rightarrow ClO + O_2 \qquad (17)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (18)$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (19)$$

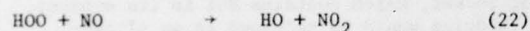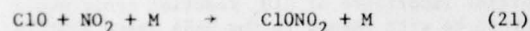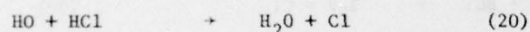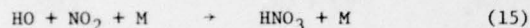$$HO + HCl \rightarrow H_2O + Cl \qquad (20)$$

The initial importance of ClO_x reaction cycle was thought to be with regard to the NASA Space Shuttle booster rocket, which contains HCl in its exhaust. Thus, chlorine would be released in an already "buffered" form (HCl) in the stratosphere, but reaction 20 would produce the catalysts for reactions 17 and 18 until the HCl was removed by rainout. Concern about this problem (50 Space Shuttle launches per year have been estimated[21] to reduce ozone by only a small fraction of 1%) was soon dwarfed by the now famous discovery of Molina and Rowland that vast amounts of stratospheric chlorine would be released by photolysis of fluorocarbons ($CFCl_3$ and CF_2Cl_2, sometimes referred to as "Freon" or F-11 and F-12, respectively). It is this latter source of ozone reduction that has dominated public attention and research for the last two years.

Clearly, a number of substances, natural and anthropogenic, are involved in ozone chemistry. When all of the known important reactions affecting stratospheric ozone are noted, they actually number around 100 or so and involve several dozen different chemical species depending upon the details of the question one wishes to pursue. Two important general considerations deserve special attention: the complex competing relationships among the various ozone production and destruction reactions, and the uncertainties in our ability to quantitatively predict (i.e., mathematically "model") the system's behavior.

It is implicit in the above that the natural HO_x, ClO_x and NO_x systems must be "balanced" in the absence of anthropogenic influences, since there is only a fixed amount of ozone that represents the excess of ozone production over ozone loss by the

Chapman system (reactions 1 thru 4). In addition to being balanced, these systems are closely coupled, both directly and indirectly. For example, reaction 15 removes both HO and NO_2 from their respective catalytic ozone destruction cycles--reactions 7 and 8, and reactions 12 and 13. In the case of NO_2, for example, this slows down the speed of catalytic destruction of ozone, since the rate at which reaction 13 proceeds determines the amount of ozone destruction which will be realized. Reaction 13 is thus sometimes termed the "rate-limiting" step. But such a simplified view of things must be formed and interpreted only with great caution. In the simple catalytic cycles which we described above, such an analysis may be valid. But we are now beginning to recognize the complexity of the real atmospheric system. Not all of the important chemical subsystems are simple two-reaction mechanisms which proceed perhaps thousands of times before one of the constituents is removed (e.g. by $HO + NO_2 + M \rightarrow HNO_3$). Many of the reaction sequences involve half a dozen or more steps, with alternative reaction pathways at more than one point along the way. These more complex reaction sequences can be of major importance to the overall stratospheric ozone balance, and do not lend themselves to simple analysis. Complex models must be brought to bear on the problem, and their results carefully interpreted.

To resort, for the sake of example, to simple recitations of the coupling process we describe, consider that the following reactions are all of some importance in attempting to model stratospheric chemistry:

$HO + NO_2 + M$	$\rightarrow$	$HNO_3 + M$		(15)
$HO + HCl$	$\rightarrow$	$H_2O + Cl$		(20)
$ClO + NO_2 + M$	$\rightarrow$	$ClONO_2 + M$		(21)
$HOO + NO$	$\rightarrow$	$HO + NO_2$		(22)
$HO + HOO$	$\rightarrow$	$H_2O + O_2$		(23)
$NO + ClO$	$\rightarrow$	$NO_2 + Cl$		(24)

It is clear that, in addition to ClO_x, HO_x and NO_x directly reacting with ozone, the reaction of many forms of these species directly with each other may be of importance. The importance of reactions 15 and 20 was discussed earlier. Including reaction 21 is of major importance to those attempting to understand the effects of fluorocarbon release on ozone, and is presently responsible for a reduction of the calculated ozone-destruction effectiveness of chlorofluorocarbons by about a factor of 2 (i.e. to 50% of what would be computed without this one reaction). Reaction 22 is important now because it had previously been thought to proceed at a rate approximately 20 times slower than was recently measured by Howard and Evenson[22]. Using the newly-measured rate, the calculated effects of aircraft are dramatically reduced. (The rapid rate of this reaction also causes a re-evaluation of other important reaction rates which had earlier been estimated by interpreting experiments providing only data on ratios of the rate constants. Thus, the measurement of Howard and Evenson has a major effect on several rate constants.) Reaction 23 terminates the HO_x catalytic ozone-destruction chain but, since a balance among ozone destruction mechanisms must be maintained, the recently accepted[27] slower rate for this reaction shifts a significant amount of calculated ozone

reduction from NO_x to HO_x. Reaction 24 short-circuits both the NO_x cycle and the ClO_x cycle, and is thus of importance to both.

With the kinds of complexity described above, simple uncertainty analyses should not be expected to produce meaningful answers. Indeed, it is instructive to note that the large uncertainties now recognized in our understanding of stratospheric chemistry were not explicitly recognized in either the CIAP, NAS, COMESA or COVOS reports discussed earlier. At their writing, attention was focused on atmospheric transport uncertainties, which accounted for most of the uncertainty assigned to the final result in both the CIAP and NAS studies. In large part, this was due to a conceptual difficulty: one can measure the uncertainty of something relative to a "true" value, but if one doesn't know "the truth," how can one estimate the uncertainty of one's limited knowledge? To our knowledge, only one serious attempt at an uncertainty estimate has been published in the referred literature, that by Duewer et al[23]. (For a complete discussion, one is also referred to Johnston and Nelson's commentary[24] on that paper, and the accompanying reply by Duewer et al[25].)

Duewer et al. present a series of model experiments in an attempt to examine the sensitivity of model-calculated ozone reduction for a given stratospheric NO_x injection. The model did not include chlorine reactions, and used the reaction-rate estimates and uncertainties assigned by Hampson and Garvin[26], which were the basis of CIAP and NAS computations as well as the principal source of data for modeling studies under COMESA and COVOS. In brief, they found a startling sensitivity to uncertainties, even when only a small number of rates were considered. Carefully stressing that they did not really believe that it was realistic, they showed that if one were to minimize the ozone-destroying effect of only three reactions (but remain within the bounds of uncertainty earlier established for each reaction by Hampson and Garvin), flight of "Concorde-like" (our term) SST aircraft would actually increase ozone. Adopting the 1976 NAS-assumed[27] value for only one of these reactions (here denoted reaction 23) caused a reduction in the calculated effectiveness of stratospheric NO_x by a factor of 2. Their conclusions pointed up the caution which must be used in this new area of atmospheric science, and indicated that more accurate determinations of much of the existing chemical reaction-rate data are sorely needed, for $HO_2 + HO_2$ and our reactions 8, 15, 22 and 23. The reaction $HOO + NO_2 \rightarrow HOONO_2$ was not included in this study, and may also be of importance.

Transport Parameterizations

The study of aircraft effects on ozone is considerably different from that of fluorocarbons on ozone in regard to the importance of assumptions made about atmospheric transport. Briefly, fluorocarbons are inert at altitudes below about 30 km, above which they are photolyzed by solar ultraviolet radiation to produce chlorine. The length of time it takes the average fluorocarbon molecule to reach this altitude is quite long, on the order of several decades. The active life of the chlorine atom in terms of ozone destruction, however, is much shorter, on the order of a couple of years. The former (upward) transport time results from the fact that surface releases must first uniformly mix in the lower atmosphere, slowly "filling it up" to some equilibrium level, before the

material can reach upper stratospheric regions in significant amounts. Thus, the equilibrium amount of inert fluorocarbons is first realized in the lower atmosphere before it is achieved in the upper regions of the stratosphere. Once a chlorine atom is released in this upper stratospheric source region, however, an inverse situation exists. The atmosphere then fills "from the top down." Since the chlorine is only active in the stratosphere-- which constitutes about 10% of the atmospheric mass--it is relatively rapidly (on the order of 2-3 years) removed to the troposphere and rained out (as HCl). The details of the upward and downward transport are of little importance. Whether it takes 90 years or 100 years for the average fluorocarbon molecule to reach heights where it may be photolyzed is clearly irrelevant. Similarly, estimates of downward transport of such high-altitude "injections" (via photolysis) of chlorine have been made with an accuracy sufficient to establish the magnitude of chlorine destruction that will occur. For fluoro-carbons, then, uncertainties in chemistry (and particularly in the validity of the assumption of their lower-atmospheric inertness) far outweigh any transport uncertainties, owing to the altitude of the "injection" of the active species.

Such is not the case for aircraft-NO_x injections which take place between about 10 and 18 km. This is the region of the atmosphere where transport uncertainties are greatest (for consideration of average global-scale mixing). Here the tropopause is defined as the dividing line between stratosphere above and troposphere below, and its location is usually assigned to a well-defined inflection point in the lapse rate. Figure 2 shows a good example of why one cannot term the tropopause well behaved: it is highly variable in space and time.
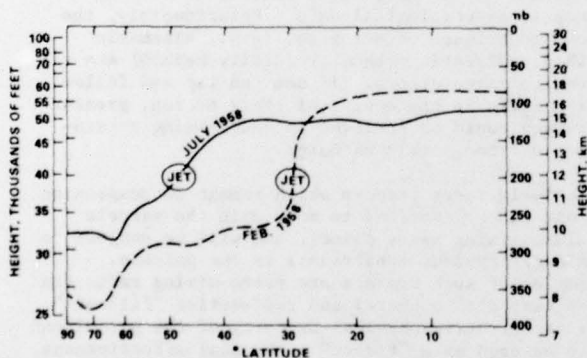

Figure 2: Monthly mean tropopause, longitude 78°W, Northern Hemisphere.

Any model which seeks to assess the amount of ozone destruction associated with aircraft-NO_x injections must account for the rate at which the NO_x is re-moved (upward or downward) from the region of in-jection. Simplistically, on a global-average scale, upward transport from aircraft flight altitudes toward the region of high ozone concentration will result in ozone destruction, while downward or quasi-horizontal transport has the opposite effect. Thus, transport uncertainties can place a funda-mental limit on our quantitative understanding of aircraft effects.

Small-scale turbulence is one form of atmospheric motion that immediately comes to mind, but a proper analysis must also take into account mean meridional (north-south) motions, transient disturbances propagated upward from the troposphere (as from hurricanes), "gravity waves" and "quasi-stationary waves." Unfortunately, these motions do not operate independently, and again we are forced to employ mathematical models as predictive tools. Atmospheric-circulation models which are based on fundamental physical principles, and explicitly treat time-dependent motions in all three dimensions are called general-circulation models (GCMs). Some GCMs have been shown to represent the major atmospheric processes reasonably well in the region of our interest, as described by Smagorinsky[28]. (An ex-cellent review of the general field is also provided by the National Academy of Sciences[29].) GCMs are, unfortunately, massive and complex constructs which require at least several years of dedicated effort to properly design, construct and test before they can be used. Calibration tests have demonstrated that some of these models are able to simulate the behavior of atmospheric trace substances well enough to give confidence in their usefulness as predictive tools, and at least one (that described in reference 30) is currently being used at the Geophysical Fluid Dynamics Laboratory to predict dispersion and trans-port of high-altitude aircraft exhaust (private communication, J. D. Mahlman, 1977). The complexity of these models, however, coupled with their present inability to include many chemical reactions owing to computational size limitations, naturally leads to a desire for physically and statistically valid simplifications. One example of a simplified three-dimensional model is the quasi-geostrophic spectral model of Cunnold et al[31]. The low spatial resolution of such models, however, gives cause[30] for concern over their ability to adequately simu-late stratospheric behavior, since a significant amount of tropospheric kinetic energy is found on relatively small scales (above planetary wave number 6) and may significantly affect stratospheric circulation.

Another possible method to reduce computational complexity is to "average out" presumably less important motions, as is done in "two-dimensional" (2-D) and "one-dimensional" (1-D) models. The 2-D models explicitly treat only north-south and ver-tical motions, whereas 1-D models explicitly treat only the global-average vertical motion components.

Unfortunately, there has yet to be found an incon-trovertibly "correct" basis for the "parameteri-zations" which must be employed in simplified models of any dimension. The more simplified the model, the more highly parameterized it must be, and the more cautious one must be in interpretation and use of its results. Simplified models are largely based on intuition and phenomenology.

The most widely used models for studies of aircraft effects have been the 1-D models. These are highly parameterized transport models but, because of their ability to explicitly include virtually all important chemistry, they have proven highly useful. Most employ a "vertical eddy-diffusion" formulation, which describes global- (or hemispheric-) average net vertical transport of substances, and is based on an engineering fit of some kind to a trace-constituent concentration profile (the "tracer").

(The eddy-diffusion coefficient, empirically determined by a fit to actual data, when multiplied by the local mean tracer gradient, is equal to the local tracer flux.) An excellent description of the derivation of one such eddy diffusion coefficient (not specifically designed to treat aircraft effects) is given in Appendix B of reference 27. (The "stretching," "smoothing," "adjusting," "fitting," "shifting" and "assuming" described therein are instructive, especially for their implications.)

Unless an eddy-diffusion coefficient is specifically derived from mathematical inversion of a truly inert atmospheric tracer--and none presently employed falls into this category--it is not consistent to continue to employ the diffusion coefficient after changing any chemical reaction subroutines which directly or indirectly affect the calculated concentration of the "tracer." For example, diffusion coefficients based on inversion of the concentration vs. altitude profile of CH_4, when the assumed rate of reaction for HO + HOO was 2×10^{-10} mol cm^3 sec^{-1}, are no longer strictly valid when the assumed reaction rate is changed to 2×10^{-11}. (Reaction with HO is an important upper-stratospheric loss mechanism for CH_4.) This point of internal inconsistency of the present approaches to 1-D modeling is apparently of little concern to most researchers. Since the implied uncertainties which result have never been explicitly explored, we again point out the need for caution in interpretation of the results.

More to the point, however, is the fact that there does not presently exist a data set which can be used to derive an adequate parameterization of transport in the 10- to 20-km region. This arises from the fact that the data set should concern a species whose chemical life is appropriately matched to transport times in that region. The concentration profiles which form the data set must be highly accurate, and a globally representative set acquired over at least several years must be available. In addition to those requirements, all significant chemical sources and sinks of the constituent must be known, in order not to falsely ascribe, for example, concentration decreases arising from unknown chemistry to rapid transport out of the region under study.

When all is said and done, the 1-D models must be regarded as extremely powerful tools, if properly used. They have been used to establish the likely importance of individual chemical reactions, the apparent sensitivity of stratospheric chemistry to uncertainties in reaction rates, and the approximate natural concentration of atmospheric trace constituents. Unfortunately, in the case of aircraft, the state of our knowledge (and the increasingly decreasing calculated sensitivity of stratospheric ozone to NO_x injections) forces us to increase our emphasis on the importance of developing higher dimensional models. Though it is not clear that 2-D models are more accurate than 1-D models in this context, the ability in principle to more completely treat transport in the tropopause region is the principal justification for their use.

We have to date relied principally on the work of two groups for 2-D modeling studies in HAPP. The latest pertinent results of these efforts are described by Widhopf[32] and Hidalgo and Crutzen[33]. Again, the principal difficulty with regard to transport is the lack of fully satisfactory means for establishing the validity of the models' calculated transport of trace constituents. In the case of 2-D models mentioned above, mean meridional motions are inputs, and three sets of eddy diffusion coefficients (north-south, vertical, and north-south/vertical coupling) must be employed, all of which must be, of course, mutually consistent. There is no well accepted set of such data, and (as in the case of 1-D models) considerable intuition must be relied upon. It is interesting to note, at this point, that the need for measured data is approximately the same for the validation of all models: 1-D models need the same raw data set as 3-D models, contrary to intuition, if they are ever to be "validated" to the same degree of confidence. The only difference is the degree of averaging of the raw data.

As stated earlier, one of the least understood aspects of stratospheric pollution studies is the exchange of air across the tropopause, i.e., between the stratosphere and the troposphere. Such exchange, in the downward direction, constitutes an important removal mechanism for pollutants injected or formed in the stratosphere (e.g., radioactive debris or HNO_3), and in the upward direction can be a source of stratospheric pollutants (e.g., NO_x formation from N_2O). It is appropriate to discuss this matter more fully.

A direct calculation of stratospheric-tropospheric mass exchange is possible in principle if one has a knowledge of the distributions of vertical velocity and concentration. But it is almost impossible to directly observe vertical velocity over the large scales of transport which are important, and so its value has to be inferred by calculations using synoptic meteorological data. Unfortunately, the known techniques of doing so, (e.g., kinematic method, adiabatic method, vorticity method) are all prone to large errors. If one can tag and follow air parcels in the course of their motion, greater accuracy could be achieved in determining stratospheric-tropospheric exchange.

Relatively inert tracers which remain in suspension in air can be expected to move with the parcels (unless mixing takes place), and will be subject to the same physical constraints as the parcels. Examples of such tracers are ozone mixing ratio (in the lower stratosphere) and radioactive "fallout." Any conservative physical property of the parcel can also be used as a "tracer" with equal effectiveness, in principle. One such property is the so-called potential vorticity, which is conserved during isentropic motion.

Mathematically, potential vorticity is a product of the measures of the resistance of an air parcel to vertical and horizontal displacement. Hence, heating above and cooling below (i.e., increased vertical stability) increases the potential vorticity. Thus the heating source of the ozone layer generates large values of potential vorticity in the stratosphere. Conversely, heating from below decreases potential vorticity. This is the case for the troposphere, which is heated by the Earth's surface.

Reed[34] and Reed and Danielsen[35] have shown that the stratospheric values of potential vorticity exceed the tropospheric values by one, two or three orders of magnitude. This circumstance can be used to

trace intrusions of stratospheric air into the troposphere and vice versa; i.e., since each air parcel conserves its value of potential vorticity, the air of stratospheric origin can be readily identified even after it is considered part of the troposphere.

Danielsen[36], using isentropic analyses, studied stratospheric-tropospheric exchange. He showed, from in-situ measurements of radioactive fallout, that the tropopause "folding" phenomenon was predictable, that it accompanied large-scale cyclogenesis and that the stratospheric air could be identified by both radioactivity and potential vorticity. Later[37] he established that the radioactivity and ozone measurements were well correlated.

Thus, potential vorticity, a purely meteorological quantity, can be used to analyze stratospheric-tropospheric exchange without incurring the large expense of making synoptic observations of ozone or radioactivity.

An effort has been initiated under the sponsorship of the High Altitude Pollution Program to develop an objective methodology for the calculation of actual stratospheric-tropospheric mass exchange by exploitation of the "tracer" characteristics of potential vorticity. It is expected that development of this data set, using worldwide 12-hourly radiosonde data, will provide a truly meaningful data base for use in the development and test of models which more realistically represent transport in the region of the tropopause. The task is a difficult and challenging one, which will take several years. We are confident, however, based on the work of Danielsen[37], that the undertaking is worthwhile.

Present Understanding

Tables 1 and 2 and Figure 1 summarized the status of understanding of aircraft effects on ozone derived from the CIAP, NAS, COMESA and COVOS studies. Since the publication of those four reports, little additional information has been gained which permits major modification to the approximations they employed to represent atmospheric transport. The most detailed work performed in this respect was mentioned earlier (see Appendix B of reference 27), and Chang et al[38] have adopted this slightly modified vertical transport estimate in their modeling efforts. What is significant, however, are the major modifications to our understanding of aircraft effects on ozone which have arisen in the chemistry area. These changes involve two principal factors: a better appreciation of the uncertainties in our knowledge, and a reduction in the uncertainty in several chemical reaction rates by virtue of their measurement in the laboratory; and the discovery of the importance of chlorine in the stratosphere, with its direct and indirect influences on calculations of aircraft effects.

To best understand the impact of changes which have taken place in chemistry, Table 3 lists 11 individual changes which have been made (private communications, D. Wuebbles, 1976, and J. Chang, 1977) to one model discussed in Chang and Johnston[39]. After each change, we note (to only two significant figures) the newly computed global reduction in ozone which is calculated for a NO_x injection of 2,000 mol cm^{-3} sec^{-1} (2.5 x 10^9 kg/year) into a 1 km thick layer centered at 17 or 20 km.

Table 3: Effect of Various Chemistry Changes on Computed Global Ozone Reductions for NO_x Injections at 17 km and 20 km (see text)

Change Made	Computed Ozone Reduction	
	17 km	20 km
Start (1974-reference 39)	4.8	~11
New Chang eddy diffusion[27]	5.4	12
$(N_2O + h\nu)$ changed from Bates and Hayes[40] to Johnston and Selwyn[41]	5.3	12
Add "smog" reactions: $OH + CO_2$, $O + CH_4$, $H_2O_2 + O$, $HO_2 + h\nu$, $OH + CH_4$	4.8	11
$OH + HO_2$ (2 x 10^{-10} → 2 x 10^{-11})	2.1	6.4
$OH + HNO_3$ (1.3 x 10^{-13} → 8.9 x 10^{-14})	2.0	6.0
$NO_3 + h\nu$ (branching, $NO + O_2$ → 2/3($NO_2 + O$), 1/3($NO + O_2$))	1.6	5.2
$O(^1D)$ reactions with N_2O, N_2, O_2, CH_4, H_2O changed from Hampson and Garvin recommendations[26] to Streit et al recommendations[42]	1.5	4.9
$OH + NO_2 + M$ (Tsang[43] → Anastasi et al[44])	1.5	4.8
$HO_2 + HO_2$ (3 x 10^{-11} exp ($^{-500}$/T) → 1.7 x 10^{-11} exp ($^{-500}$/T))	1.2	4.3
$HO_2 + O$ (8 x 10^{-11} exp ($^{-500}$/T) → 3 x 10^{-11})	1.2	4.2

Note that the data in Table 3 still do not directly address stratospheric chlorine, which is now believed to be naturally present at a level of about one part per billion (ppb) in the stratosphere, and is increasing owing to photolysis of fluorocarbons released at the surface in the past decade or so. Including about 1ppb of chlorine in the above model reduces the ozone reduction for the respective 17- and 20-km NO_x injections from about 1.2% and 4.2% to about 0.7% and 3.3%, respectively. This arises from the slowing down of the NO_x catalytic cycle (reactions 12 and 13) by reaction 24. In turn reaction 21, when subsequently included, tends to increase somewhat the effects of the NO_x catalytic cycle again, since ClO is tied up as ClONO$_2$, thereby slowing reaction 24 relative to reaction 12. (Though reaction 24 actually reduces the amount of NO_x available for ozone destruction, the increased speed of reaction 12 more than compensates for this.)

Increasing amounts of chlorine in the stratosphere are physically inevitable for the next decade or so, since the fluorocarbons which will cause them have already been released. (Even if stopped instantly, fluorocarbon releases of the past will act to increase the stratospheric chlorine content for about a decade as they are slowly transported upwards, as discussed in the earlier section on transport.) Realistically, it is likely that the chlorine content of the stratosphere will increase for a longer

period, owing to the economic and political diffi- culties in developing and implementing adequate substitutes on a world-wide scale. Thus, any model of NO_x effects from aircraft injections cannot be realistic without incorporating chlorine effects. But it is difficult to gauge future stratospheric chlorine contents accurately, and about all that can intelligently be said is that for about the next 30 years at the very least, the effects of strato- spheric chlorine will reduce the sensitivity of stratospheric ozone to aircraft injections of NO_x.

Before discussing Figure 3, it is important to recall the comments in the earlier section on chemistry about the major significance of Howard and Evenson's recent determination[12] of the very rapid rate for reaction 22 (HOO + NO), and its implica- tions. The magnitude of this effect is clear from examination of Figure 3, which presents a graphic display of the data in Table 3 and extends that data to include consideration of stratospheric chlorine and the new data of Howard and Evenson. Figure 3 is intended to illustrate how one model[39] has been affected by knowledge gained in the last two or three years. It is essential--and this cannot be stressed enough--that we remember that there are still major uncertainties and, likely, real gaps in our knowledge. It is possible--even likely--that some of the "revised" data shown on Table 3 and Figure 3 will be revised once again. In addition, the transport coefficient used in the model can have a major impact on its output. If the "Hunten"[45] eddy-diffusion coefficient is used in this model, the 20-km injection of Figure 3 is calculated to reduce ozone (as shown by the letter "H" on Figure 3), and the production of ozone by 17-km NO_x injec- tions is reduced by about a factor of 4. Never- theless, one cannot escape the fact that, since the completion of the CIAP, NAS, COMESA and COVOS studies, new data indicate strongly that the ozone layer is markedly less sensitive to injections of NO_x by SSTs than was concluded by these studies. At this point, the sign of the effect (i.e. ozone decrease or increase?) is not at all clear.
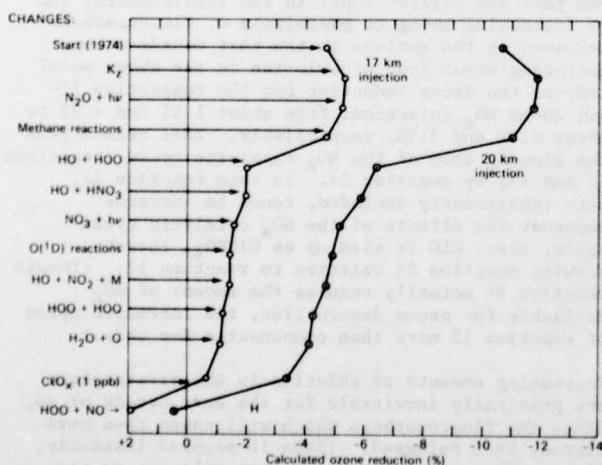

Figure 3: Effects of changes in model assumptions (ordinate) on calculated global-ozone reduction (abscissa) for a NO_x injection of 2.46×10^{12} gm/yr at indicated altitude (after Chang[39]).

With regard to subsonic aircraft, much the same can be said, though perhaps with more confidence. Figure 4 is essentially the same as Figure 1, but we have added a curve which is broadly representative of the results of studies recently described by Widhopf[32], Hidalgo and Crutzen[33], and those at the Lawrence Livermore Laboratory (private communication, D. Wuebbles, 1976). These results have recently been well summarized in detail by Oliver et al[15], and do not account for chlorine in the stratosphere, or for the changes required to take account of the results of Howard[22] and Evenson. It is clear, however, that according to our best present under- standing, the effect of subsonic (i.e. below about 15 km) flight is not such as to cause ozone reduction, but might be to even slightly enhance ozone. Con- sidering the implications of including effects of chlorine and the results of Howard and Evenson on the conclusions implicit from Figure 4, the case against ozone reduction resulting from subsonic aircraft operations is considerably strengthened.
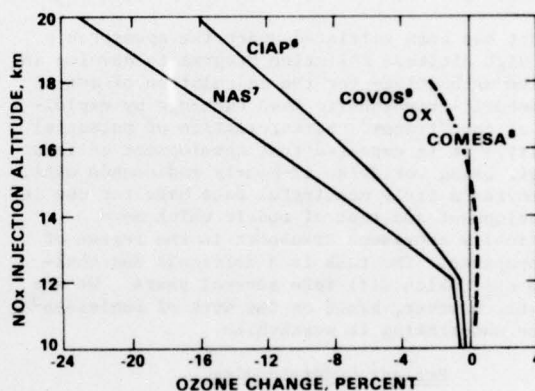

Figure 4: Same as Figure 1, but dashed line broadly represents results of later calculations before accounting for the presence of stratospheric chlorine and the recently measured[22] fast rate for HOO + NO (see text and Figure 4; after Oliver et al[15]).

Uncertainty Predictions

It was mentioned earlier that an analysis of the uncertainties in model predictions of effects on ozone is difficult. One approach that has proven quite useful is that of Duewer et al[23] discussed briefly in the section on chemistry. An inherent difficulty in any such attempt is the extreme complexity of the models with which we must deal. They may involve about 100 nonlinearly coupled reactions, and dozens of different reacting species. What we really seek is a method of assigning real- istic probability distributions to the error in- herent in each input parameter. But these are not solely random errors. They also include systematic errors, not readily subject to assignment of error bounds. Inductive reasoning simply does not lend itself to straightforward error analysis.

Whereas Duewer et al used intuition and a pains- taking trial-and-error process in their analysis, Stolarski et al[46] have performed a different anal- ysis of errors (in this case, for fluorocarbon studies, but the general results and methodology are applicable to NO_x studies). They provide results in reasonable agreement with the brief analysis of uncertainties describe in reference 27. They

employed a 1-D model and assigned each reaction rate an uncertainty based largely on estimates of Hampson and Garvin[26]. The form of this assigned uncertainty was that of a normal (Gaussian) distribution. They then performed several hundred model runs, with each of the 48 reaction rates being individually varied according to its assigned probability distribution, and a Monte Carlo scheme employed to propagate the uncertainties through the entire model calculation. They concluded that a reduction of all rate measurement uncertainties to $\pm$15% would result in an overall uncertainty of $\pm$ 30% for a given calculation of ozone reduction, but that with present uncertainties, "the correspondence to a Gaussian is better on the high side, where a one-sigma uncertainty of a factor of 2 is found." Intuitively we would expect a somewhat greater uncertainty on the low side (i.e. less ozone reduction for a given ClO_x injection) since, after all, less-than-zero ozone reduction is possible, but reference 46 gives no further details.

The approach of Stolarski et al[46] appears at first glance to be more rigorous than that of Duewer et al[23], but we question the validity of assigning probability distributions, as they have done, to uncertainty estimates which are almost surely in error for systematic reasons, and not for reasons of a lack of measurement precision. With the assumption they have employed, what does the answer really mean from a practical viewpoint? We believe both methods to be useful, especially as tools for management of scientific programs which attempt to assess the stratospheric impact of various anthropogenic emissions.

While the above uncertainty studies are useful as management tools, we believe that, given the present lack of measured data on atmospheric parameters which affect ozone (including ozone itself), and the inductive nature of the fundamental problem under investigation, neither study can be said to have given a true measure of uncertainty (nor do they so claim). This is dramatically borne out by the analysis of Duewer et al which showed the impossibility of ruling out even highly improbable combinations of assumed reaction rates by comparing model predictions with available atmospheric measurements. The precision and accuracy of the existing field-measurements data, coupled with the inherent (and frustrating) natural variability of meteorological parameters, render such attempts useless except to point out grossly erroneous formulations. This capability to "bound" the problem should not be treated lightly, however, as it can occasionally prove quite useful. An example of an analysis of atmospheric measurements which proved useful in that manner is described by Ackerman et al[47].

Gaps to be Filled

We are able to identify a number of significant areas of uncertainty which, among others, must be addressed if our understanding of the effects of aircraft-NO_x emissions on stratospheric ozone is to be on a solid foundation. These are outlined below, in no particular order of importance:

There is an essential need for an improved atmospheric data base, for use in testing and calibrating atmospheric models. For aircraft studies, we particularly need data on the relationships among various individual species of the NO_x family in the presence of ozone. This calls for truly simultaneous (in space and time) measurements of the NO_x constituents and ozone at various latitudes and seasons, as a function of altitude to at least 35 km, and preferably higher in order to acquire data in a region of photochemical equilibrium. Availability of such data, really an extension of the ongoing measurements described by, for example, Evans et al[48], is an absolute prerequisite to definitively establishing the role of aircraft-NO_x emissions in regard to stratospheric ozone.

As discussed in the section on transport, we see a real absence of data which may be used to emulate or parameterize transport in the critical altitude region of 10 to 20 km or so. Discrepancies in model results due only to transport, such as those shown on Figure 3, may turn out to be a fundamental limitation of our ability to predict effects of aircraft on ozone. If Figure 3 were to represent the "final" state of things (which we suspect it does not), the difference in the calculated effect on ozone due only to use of two different transport parameterizations would be intolerable. It may mean the difference between predicting adverse and insignificant effects on ozone. Presently, there is no rigorously defensible means of determining which of the two parameterizations shown (of the many available) is "more valid."

Water-based constituents—the HO_x "family"—play an important role in the stratospheric ozone balance. These constituents also directly and indirectly bear upon the sensitivity of stratospheric ozone amounts to changes in stratospheric concentrations of other species, including ClO_x and NO_x. Finally, they indirectly couple ClO_x and NO_x ozone cycles. Yet we do not have a reasonably good basis for assigning a value to the amount of water vapor in the stratosphere. The recent comprehensive review of Harries[49] demonstrates the point quite adequately. There are, then, two critical needs with regard to water vapor measurements: development of instruments capable of measuring water to heights of at least the stratopause (about 50 km), and accomplishment of the measurements themselves to provide a reasonable global stratospheric inventory of water. As a minimum initial step, lower stratospheric water measurements initiated by Mastenbrook[50] must be continued and expanded to several additional sites.

Not discussed elsewhere here, it is necessary to point out that the uncertainties in determination of aircraft exhaust-NO_x concentrations first pointed out by McGregor et al[51] have yet to be resolved. From our extensive discussions about the validity of their data, we can only conclude that one is neither able to dismiss it as inaccurate nor, conversely, can one show the shortcomings of the technique (if there are any). Accordingly, one must acknowledge an uncertainty in the NO_x emission rates assigned to aircraft cruise operations. This uncertainty likely ranges somewhere between the order of tens of percent for "dry" engines and several times (up to a factor of 4 or 5) for engines which employ afterburning during cruise. Without knowing the reason for the discrepancy one cannot be more precise.

As stated several times herein, the recent work of Howard and Evenson[22] carries major implications with regard to our understanding of the maintenance of the stratospheric ozone balance. This work must be confirmed by an independent experiment. In

addition, the work of Duewer et al[23] points up the crucial role played by a number of reactions in which the HO_x species participate. These also need to be measured--some have not--and/or be independently verified.

We do not presently have a reasonable idea of the global ozone inventory, or its variability with altitude, season and latitude. This is a critical void and should be rectified as soon as possible. NASA is in the process of attempting to analyze data acquired since 1970 on its NIMBUS 4 satellite, but the complexity of such a task ("after the fact") makes the date of availability of this information uncertain. FAA's HAPP is sponsoring a study of the feasibility of acquiring global total ozone data from the Department of Defense Block 5D Satellite; ozone data from this study are not assured, because of the exploratory nature of the effort. We turn, then, to the Ozone Data for the World, published under the auspices of the World Meteorological Organization[52]. But, as the spirited discussions at the Scientific Seminar on Stratospheric Monitoring (Paris, France, March, 1977) showed, there are a number of problems in actually trying to use this data, all of which is always labelled "preliminary." Clearly, the lack of validated, carefully analyzed data on the very substance at the center of all stratospheric studies is a situation which cannot be tolerated if the subject is to be taken seriously.

In the section on chemistry, we alluded to the complexities of the stratosphere's chemical system, the number of circuitous feedback paths, and the nonlinear nature of the system. We also later made reference to the complexities of stratospheric transport; Scorer[53] has pointed out the "layering" that can take place in this regard. In our view, there is a deep-seated need for exploration of the effects of these factors in models. Instead of being satisfied with accepting the results of models which compute results based on smoothly varying temperature and concentration profiles for all species, we must determine the sensitivity of these calculations to the jagged profiles that we know from actual measurement to be more realistic. It could turn out that nonlinearities of the stratospheric system will produce surprising results from such an analysis.

Finally, we note here the need to continue to use and improve upon the uncertainty analyses described earlier. It would be helpful if an analytic technique could be developed which could be economically employed to determine the overall sensitivity of a model output to changes in a given input parameter, especially if all other identifiable uncertainties were properly considered in the process. That is, while it is helpful to know the sensitivity of the output to a change in one input, all others being held fixed, this is not the complete story. The nonlinearity of these models could be such as to make a model appear to be insensitive to variations in one parameter, but if that parameter and another are simultaneously varied, the results might be vastly different. With as many uncertainties in input parameters as have already been discussed, it should not be surprising that we call for development of such an analytic capability.

Most of the above research needs are presently being addressed, in one form or another. Major active programs in the United States include those of the Environmental Protection Agency (with regard to engine emission-rate measurement and fluorocarbon chemistry), the National Aeronautics and Space Administration (having a major research effort in this field), National Oceanic and Atmospheric Administration (especially through its Boulder Laboratories, the National Weather Service and its Geophysical Fluid Dynamics Laboratory), the National Science Foundation (through its support of academic atmospheric sciences research generally, and of the National Center for Atmospheric Research), and the Federal Aviation Administration (through its High Altitude Pollution Program). On an international level, there is considerable work in France and the United Kingdom, of which we are kept abreast through arrangements under the Tripartite Agreement on Stratospheric Monitoring[14], and a number of specific bilateral agreements. The recent decision of the International Civil Aviation Organization to form a Committee on Aircraft Emissions chartered, among many other things, to make recommendations on stratospheric emission standards, is a good example of the seriousness of purpose which the aviation community feels in regard to these questions. Lastly, we must point to the developing program of the United Nations Environment Programme (UNEP) in the field of stratospheric ozone. It is strongly hoped that UNEP will be successful in catalyzing the international scientific cooperation, especially with regard to atmospheric monitoring, that is so clearly necessary for proper understanding of these matters.

Concluding Remarks

From the preceding discussion, it should be evident that a number of significant changes in our understanding have taken place since the completion of the CIAP, NAS, COMESA and COVOS studies. (A detailed summary of our understanding at the time of these studies (August, 1975) may be found in reference 54.) The existence of this new data should not be allowed to create an atmosphere of complacency, however. Much of the information described above, especially with regard to new chemical reaction-rate data, needs independent verification before it can be accepted with confidence. Further, in the previous section we outlined some of the major gaps which still exist in our understanding. Future data may not be as encouraging--from the aviation community's viewpoint--as has been the case with data acquired in the recent past.

We also hasten to point out that this discussion has focused on NO_x effects on ozone. What about those of water? The natural ozone production-destruction system must remain balanced, and the fact that ozone is less sensitive to NO_x increases than previously believed means it must be more sensitive to other perturbations. ClO_x has taken up some of the "slack," and HO_x has absorbed the rest. Thus, detailed evaluation of perturbations to ozone from water in aircraft exhaust needs to be considered once again. (Preliminary analysis of the sensitivity of ozone change to aircraft emissions of water, taking into account the most updated chemistry, indicates (private communication, J. Chang, 1977) only a modest effect.)

With the limitations we have described here in mind, and drawing attention to the comprehensive summary of effects prepared by Oliver et al[15], we note the conclusions we believe may be drawn:

1. Realistic projections to 1990 of air traffic growth for the world _subsonic_ fleet of aircraft indicate that ozone will not be significantly affected by those aircraft, with a marginal increase in ozone now being actually predicted.

2. Furthermore, analysis of the effects of _subsonic_ aircraft emissions (i.e. those below a nominal 15-km altitude) indicates, contrary to previous studies, that given our present understanding subsonic aircraft NO_x-emissions cannot forseeably result in ozone reduction irrespective of fleet size (within reasonable bounds).

3. Earlier estimates[6,7,8,9] of ozone reduction from _SST_ emissions of NO_x at 17 to 20 km appear to have been substantially in error. Based on simple 1-D models, our present understanding leads to predicted ozone perturbations of an absolute magnitude markedly smaller than given previously in these studies and outside their ranges of estimated uncertainty (if any were given).

4. For the first time, we can state that it is questionable whether NO_x emissions from "Concorde-like " SSTs (flying at about 17 km) reduce ozone at all. Present results, of 1-D models which consider both tropospheric and stratospheric chemistry, indicate that they do not, though these new data need verification before we can completely accept this important finding.

5. Similarly, the effect of NO_x emissions from aircraft cruising at 20 km is in doubt, though small ozone reductions for very large fleets of such aircraft are still predicted by some models.

6. 2-D models (and 3-D models, if possible) must be used to corroborate the present results from 1-D models regarding SST perturbations; the ability of 1-D models to predict the direction of ozone perturbations (i.e. increase or decrease) is severely strained when the absolute magnitude of the effect is near zero, and latitudinal variations in average ozone effects may be of importance in a complete assessment of the problem.

7. There is a clear need for more data on trace constituents in the atmosphere (especially simultaneous measurements of NO_x species, and measurements of HO_x species), for laboratory measurements of critical chemical reaction rates, for development and use of uncertainty analysis tools, and for a better understanding of transport in the 10- to 20-km altitude region.

In summary, present understanding indicates that there is no imminent threat of ozone reduction from any type of existing aircraft, though substantial uncertainties remain. Thus there appears to be no immediate requirement to develop regulations which would mandate a reduction in cruise-altitude emissions of subsonic or supersonic aircraft. There is a clear necessity for continued study to reduce remaining uncertainties, and to establish a uniform and internationally agreed accurate NO_x emission measurement scheme. Building a framework for regulation (if necessary) of future types of high-

altitude aircraft, such as those frequently referred to as a "second-generation SST," or the even higher flying hypersonic transport (HST), is also necessary. Activities of the new ICAO Committee on Aircraft Emissions should be encouraged to proceed in an orderly fashion along these lines.

References

1. McDonald, J., Presentation before the Department of Commerce Technical Advisory Board on Environmental Aspects of the Supersonic Transport, Boulder, CO, March 17-18, 1971.

2. Harrison, H., "Stratospheric Ozone with Added Water Vapor: Influence of High-Altitude Aircraft," Science, Vol. 170, 1970, pp. 734-736.

3. Man's Impact on the Global Environment, Report of the Study of Critical Environmental Problems (SCEP), Massachusetts Institute of Technology Press, Cambridge, MA, 1970.

4. Crutzen, P. J., "The Influence of Nitrogen Oxides on the Atmospheric Ozone Content," Quarterly Journal of the Royal Meteorological Society, Vol. 96, 1970, pp. 320-325.

   Crutzen, P. J., "SST's--A Threat to the Earth's Ozone Shield?" Ambio, Vol. 1, 1972, pp. 41-51.

5. Johnston, H. S., "Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from SST Exhaust," Science, Vol. 173, 1971, pp. 517-522.

6. Grobecker, A. J., Coroniti, S. C., and Cannon, R. H., Jr., "The Effects of Stratospheric Pollution by Aircraft," U.S. Department of Transportation, Washington, D.C., Rept. DOT-TST-75-50, 1974.

7. "Environmental Impact of Stratospheric Flight," National Academy of Sciences, Climatic Impact Committee, Washington, D.C., 1975.

8. The Report of the Committee on Meteorological Effects of Stratospheric Aircraft (COMESA), 1972-1975, U.K. Meteorological Office, Bracknell, 1975.

9. Comite d'Etudes sur les Consequences des Vols Stratospheriques (COVOS), Activites 1972-1976, Societe Meteorologique de France, Boulogne, 1976.

10. Smykov, V. G., "TU-144 Emissions," Report of the Fourth Meeting of the Technical Panel on Supersonic Transport Operations, ICAO Doc. 9076, 1973.

11. Rummel, R. W., "Possible Impact of Regulations on Airlines," Proc. of the Fourth Conference on the Climatic Impact Assessment Program, U.S. Department of Transportation, Washington, D.C., Rept. DOT-TSC-OST-75-38, 1976, pp. 127-131.

12. Meister, F. A., in "Panel Discussion," Proc. of the Fourth Conference on the Climatic Impact Assessment Program, U.S. Department of Transportation, Washington, D.C., Rept. DOT-TSC-OST-75-38, 1976, pp. 24-38.

13. "The Secretary's Decision on Concorde," U.S. Department of Transportation, Washington, D.C., February 4, 1976.

14. "Tripartite Agreement on Stratospheric Monitoring," Concluded among France, the United Kingdom, and the United States, May 5, 1976.

15. Oliver, R. C., et al., "Aircraft Emissions: Potential Effects on Ozone and Climate," U.S. Department of Transportation, Washington, D.C., Rept. FAA-EQ-77-3, March 1977.

16. Chapman, S., "A Theory of Upper-Atmosphere Ozone," Mem. Royal Meteorological Society, Vol. 3, 1930, pp. 103-125.

17. Johnston, H.S., "Global Ozone Balance in the Natural Stratosphere," Reviews of Geophysics and Space Physics, Vol. 13, 1975, pp. 637-649.

18. Hampson, J., "Photochemical Behavior of the Ozone Layer," TN 1627/64, CARDE, Valcartier, Quebec, Canada, 1964.

19. Hunt, B. G., "Photochemistry of Ozone in a Moist Atmosphere," Journal of Geophysical Research, Vol. 71, 1966, pp. 1385-1398.

20. Stolarski, R. S., and Cicerone, R. J., "Stratospheric Chlorine: Possible Sink for Ozone," Canadian Journal of Chemistry, Vol. 52, 1974, pp. 1610-1615.

21. Space Shuttle estimate, as quoted in Ref. 27, pp. 164-165.

22. Howard, C. H., and K. M. Evenson, "Laser Magnetic Resonance Study of HO_2 Chemistry," Paper Presented at the AGU Annual Spring Meeting, Washington, D.C., May/June 1977.

23. Duewer, W. H., et al., "NO_x Catalytic Ozone Destruction: Sensitivity to Rate Coefficients," Journal of Geophysical Research, Vol. 82, 1977, pp. 935-942.

24. Johnston, H. S., and Nelson, H., "Comment on 'NO_x Catalytic Ozone Destruction: Sensitivity to Rate Coefficients' by W. H. Duewer et al.," Journal of Geophysical Research, Vol. 82, 1977, pp. 2593-2598.

25. Duewer, W. H., et al., "Reply," Journal of Geophysical Research, Vol. 82, 1977, pp. 2599-2605.

26. Hampson, R. F., Jr., and Garvin, D., "Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry," National Bureau of Standards, Tech. Note 866, June 1975.

27. "Halocarbons: Effects on Stratospheric Ozone," National Academy of Sciences, Panel on Atmospheric Chemistry, Washington, D.C., 1976.

28. Smagorinsky, J., "Global Atmospheric Modeling and Numerical Simulation of Climate," Weather and Climate Modification, W. N. Hess, ed., Wiley, New York, 1974.

29. "Understanding Climatic Change," National Academy of Sciences, U.S. Committee for the Global Atmospheric Research Program, Washington, D.C., 1975.

30. Mahlman, J. D., "Some Fundamental Limitations of Simplified-Transport Models as Implied by Results from a Three-Dimensional General-Circulation/Tracer Model," Proc. of the Fourth Conference on the Climatic Impact Assessment

Program, U.S. Department of Transportation, Washington, D.C., Rept. DOT-TSC-OST-75-38, 1976, pp. 132-146.

31. Cunnold, D., Alyea, F., Phillips, N., and Prinn, R., "A Three-Dimensional Dynamical-Chemical Model of Atmospheric Ozone," Journal of the Atmospheric Sciences, Vol. 32, 1975, pp. 170-194.

32. Widhopf, G., Glatt, L., and Kramer, R., "A Two-Dimensional Time-Dependent Photochemical Model of the Atmosphere," Aerospace Corporation, Final Report, October 1976.

33. Hidalgo, H., and Crutzen, P. J., "The Tropospheric and Stratospheric Composition Perturbed by NO_x Emissions of High-Altitude Aircraft," Paper Presented at the Non-Urban Tropospheric Composition Symposium, Miami, FL, November 9-12, 1976.

34. Reed, R. J., "A Study of a Characteristic Type of Upper Level Frontogenesis," Journal of Meteorology, Vol. 12, 1955.

35. Reed, R., Danielsen, E. F., "Fronts in the Vicinity of the Tropopause," Arch. Met. Geophys. Biokl. A, Vol. 2, 1959, p. 1.

36. "Transport from Stratosphere to Troposphere," Mineral Ind., Vol. 33, 1964.

37. Danielsen, E. F., "Stratospheric-Tropospheric Exchange based on Radioactivity, Ozone and Potential Vorticity," Journal of the Atmospheric Sciences, Vol. 25, 1968.

38. Chang, J. S., "Coupled Chemical Kinetics and Atmospheric Transport Models of the Stratosphere," Paper Presented at the 173rd Meeting of the American Chemical Society, Anaheim, CA, March 1977.

39. The model referred to is "Model 4" in Chang, J. S., and Johnston, H. S., "The Effect of NO_x Effluents on Ozone," Proc. of the Third Conference on the Climatic Impact Assessment Program, U.S. Department of Transportation, Washington, D.C., Rept. DOT-TSC-OST-74-15, 1974, pp. 323-329.

40. Bates, D. R., and Hays, P. B., "Atmospheric Nitrous Oxide," Planetary and Space Science, Vol. 15, 1967, p. 189.

41. Johnston, H. S., and Selwyn, G. S., "New Cross Sections for the Absorption of Near-Ultraviolet Radiation by Nitrous Oxide (N_2O)," Geophysical Research Letters, Vol. 2, 1975, p. 549.

42. Streit, G. E., et al., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with O_2, N_2, CO_2, O_3 and H_2O," The Journal of Chemical Physics, Vol. 65, 1976.

43. Tsang, W., "Comparisons Between Experimental and Calculated Rate Constants for Dissociation and Combination Reactions Involving Small Polyatomic Molecules," International Journal of Chemical Kinetics, Vol. 5, 1973, p. 947.

44. Anastasi, C., and Smith, I. W. M., "Rate Measurements of Reactions of OH By Resonance Absorption," Journal of the Chemical Society, Faraday Transactions II, Vol. 72, 1976, p. 1459.

45. Hunten, D. M., "The Philosophy of One-Dimensional Modeling," Proc. of the Fourth Conference on the Climatic Impact Assessment Program, U.S. Department of Transportation, Washington, D.C., Rept. DOT-TSC-OST-75-38, 1976, pp. 147-155.

46. Stolarski, R. S., Butler, D. M., and Rundel, R. D., "Uncertainty in Stratospheric Ozone Perturbation Predictions Due to Uncertainties in Reaction Rates," Paper Presented at the International Conference on Problems Related to the Stratosphere, Logan, UT, September 15-17, 1976.

47. Ackerman, M., Frimout, D., and Muller, C., "Stratospheric Methane--Measurements and Predictions," Aeronomica Acta, A-No. 180, 1977.

48. Evans, W. F. J., Kerr, J. B., and Ridley, B. A., "Measurements of the Nitrogen Chemistry of the Ozone Layer from Project Stratoprobe," Paper Presented at the International Conference on Problems Related to the Stratosphere, Logan, UT, September 15-17, 1976.

49. Harries, J. E., "The Distribution of Water Vapor in the Stratosphere," Reviews of Geophysics and Space Physics, Vol. 14, 1976, pp. 565-575.

50. Mastenbrook, H. J., "Water Vapor Distribution in the Stratosphere and High Troposphere," Journal of the Atmsopheric Sciences, Vol. 25, 1968, pp. 299-311.

51. McGregor, W. K., Seiber, B. L., and Few, J. D., "Concentration of OH and HO in YJ93-GE-3 Engine Exhuasts Measured In Situ by Narrow-Line UV Absorption," Proc. of the Second Conference on the Climatic Impact Assessment Program, U.S. Department of Transportation, Washington, D.C. Rept. DOT-TSC-OST-73-4, 1973, pp. 214-229.

52. "Ozone Data for the World," Meteorological Branch, Canadian Department of Transportation, Toronto.

53. Scorer, R. S., "A Commentary on Ozone Depletion Theories," Atmospheric Environment, Vol. 10, 1976, pp. 177-180.

54. Broderick, A. J., "Effects of Cruise-Altitude Pollution," Journal of Aircraft, Vol. 13, 1976, pp. 817-822.